Synthesis and Mesomorphic study of Photo-Switchable Ethyl 3,5-bis(4-(4-((*E*)-(4-cyanophenyl) diazenyl)phenoxy)alkoxy)benzoate Trimers

Dissertation submitted to
Visvesvaraya National Institute of Technology, Nagpur
in partial fulfilment of the requirements for the award of
the degree

Master of Science
in
Chemistry

by

Abhilash Meher

(MS23CHM021)

under the guidance of

Dr. Susanta K. Nayak

Department of Chemistry
Visvesvaraya National Institute of Technology
Nagpur 440 010 (India)

2025

Synthesis and Mesomorphic study of Photo-Switchable Ethyl 3,5-bis(4-(4-((*E*)-(4-cyanophenyl) diazenyl)phenoxy)alkoxy)benzoate Trimers

Dissertation submitted to
Visvesvaraya National Institute of Technology, Nagpur
in partial fulfilment of the requirements for the award of
the degree

Master of Science
in
Chemistry

by

Abhilash Meher

(MS23CHM021)

under the guidance of

Dr. Susanta K. Nayak

Department of Chemistry

Visvesvaraya National Institute of Technology

Nagpur 440 010 (India)

2025

© Visvesvaraya National Institute of Technology (VNIT) 2025

Department of Chemistry

Visvesvaraya National Institute of Technology, Nagpur

Declaration

I, Abhilash Meher, hereby declare that this dissertation titled **"Synthesis and Mesomorphic study of Photo-Switchable Ethyl 3,5-bis(4-(4-((*E*)-(4-cyanophenyl)diazenyl)phenoxy)alkoxy)benzoate Trimers"** is carried out by me in the Department of **Chemistry** of Visvesvaraya National Institute of Technology, Nagpur. The work is original and has not been submitted earlier whole or in part for the award of any degree/diploma at this or any other Institution / University.

Abhilash Meher

(MS23CHM021)

Date:

Certificate

This to certify that the dissertation titled **"Synthesis and Mesomorphic study of Photo-Switchable Ethyl 3,5-bis(4-(4-((*E*)-(4-cyanophenyl)diazenyl) phenoxy) alkoxy)benzoate Trimers"** is submitted by **Abhilash Meher** in partial fulfilment of the requirements for the award of the degree of **Master of Science in Chemistry**, VNIT, Nagpur. The work is comprehensive, complete and fit for final evaluation.

Dr. S. K. Nayak

Assistant Professor
Department of Chemistry
VNIT, Nagpur

Dr. S. K. Ghosh

Professor & Head,
Department of Chemistry
VNIT, Nagpur

Visvesvaraya National Institute of Technology, Nagpur

Non – Plagiarism Certificate

Certified that M.sc dissertation titled "Synthesis and Mesomorphic study of Photo-Switchable Ethyl 3,5-bis(4-(4-((*E*)-(4-cyanophenyl)diazenyl)phenoxy)alkoxy)benzoate Trimers" submitted by **Abhilash Meher** Enrollment No. **MS23CHM021**, ID No. **30741** has been checked for plagiarism using TURNITIN software and overlap is found within prescribed limits.

A summary of the report is given below;

Abhilash Meher

(MS23CHM021)
ID No.: 30741
Date:

Dr. S. K. Nayak

Assistant Professor
Department of Chemistry
VNIT, Nagpur

Acknowledgements

I am profoundly grateful to Dr. Susanta Kumar Nayak, my esteemed mentor, for his inspiring guidance, sincere involvement, steadfast support, and valuable insights throughout the course of my M.Sc. project.

I sincerely thank Dr. Sujit Kumar Ghosh, Head of the Department of Chemistry at VNIT Nagpur, for his timely support and providing the essential facilities that played a key role in the successful completion of my project.

I am also thankful for enormous guidance by Ph.D. scholars Mr. Jyoti Swarup Thakur, Mr. Omkar Dash, Mr. Rahul D. Nagdeve, Mr. Khatendra T. Reang, Mr. Dolashiya Bhargavkumar Bharatbhai and Mr. Milan Kumar Naik throughout the course of my project.

I would like to express my sincere gratitude to all other faculty members of the Department of Chemistry at VNIT Nagpur for their generous support and valuable advice during my time at the institute.

I am grateful to DST-FIST for providing the powder XRD data (SR/FST/CSI-279/2016©), and to ANRF & MoE-STARS for supporting the project ECR/2016/001820/ MoE-STARS/STARS-2/2023-0892, which facilitated access to the Polarising Optical Microscope and Linkam hot-stage for mesophase analysis. I also extend my thanks to Dr. Ch. Ravi Shankar Kumar from GITAM University, Visakhapatnam, for his assistance with NMR data collection,

I sincerely appreciate the encouragement and support of my family members and classmates, whose presence has been a constant source of motivation.

Abstract

The liquid crystal trimers are a significant family of materials, with their uses in the rapidly expanding disciplines such as photonics, optoelectronics, and display technologies. They differ from the conventional low molecular mass LCs with respect to their structure, in which the rigid units are linked through two flexible spacers to the central aromatic core. Incorporation of a chromophore such as azobenzene enhances their potential in the development of photo-switchable devices due to the reversible $E \leftrightarrow Z$ isomerization upon irradiation of light of suitable wavelength. Keeping this in mind, a series of azo-based trimers, ethyl 3,5-bis(4-(4-((*E*)-(4- cyanophenyl)diazenyl)phenoxy)alkoxy)benzoates of various alkoxy chain lengths were (**DHB-AZN-n**, n = 4,6,8,10, and 12) were synthesized. These synthesized molecules have been characterized by FTIR, PXRD, and NMR techniques. The mesomorphic nature of these compounds have been analyzed utilizing a Polarizing Optical Microscope equipped with a hot-stage, which revealed the monotropic nematogenic behavior in the cooling cycle for all (n = 4-12). Additionally, decoxy (n = 10), and dodecoxy (n = 12) exhibited smectic A liquid crystalline phase in the cooling cycle. Furthermore, these trimers demonstrated excellent photoresponsive behavior, upon irradiation of 365 nm UV light.

List of Figures and Scheme

Figure/Scheme No.	Name of Figure/Scheme	Page No.
1.1	Phase transition in LCs	2
1.2	Cholesteryl benzoate (First LC)	3
1.3	Schematic representation of Calamitic, Discotic, and Bent core LCs	5
1.4	Texture of Nematic LCs phase	5
1.5	Texture of Smectic LCs phase	6
1.6	Texture of Chiral Nematic LCs phase	6
1.7	Texture of Columnar LCs phase	7
1.8	First Investigated LCT	8
1.9	Symmetric LCTs	9
1.10	Non-symmetric LCTs	9
1.11	Photo-isomerization process in azobenzene	10
1.12	Some of the azo based LCTs reported in the literature	11
1.13	X-ray diffraction phenomena of a crystalline substance	12
1.14	Powder X-ray Diffractometer	12
1.15	FTIR Spectrophotometer	13
1.16	POM instrument equipped with hot stage	14
1.17	NMR instrument	15
1.18	UV-Vis Instrument	16
2.1	Synthesis of azo-based Trimer molecules (DHB-AZN-n)	19
2.2	PXRD pattern of DHB-AZN-4	22
2.3	FT-IR Spectra of DHB-AZN-4	24
2.4	^{1}H NMR spectra of AZNM-4	25
2.5	^{13}C NMR spectra of AZNM-4	25
2.6	^{1}H NMR spectra of DHB-AZN-4	27
2.7	^{13}C NMR spectra of DHB-AZN-4	28
2.8	POM texture of DHB-AZN-n	30
2.9	UV-Vis Spectra of *trans-cis* Isomerization of DHB-AZN-4	32
2.10	UV-Vis Spectra of *trans-cis* Isomerization of DHB-AZN-12	32

List of Tables

Table No	Title	Page No.
2.1	The yield of the products AZNM-n	21
2.2	The yield of the products DHB-AZN-n	22
2.3	FTIR data of AZNM-n	23
2.4	FTIR data of DHB-AZN-n	23
2.5	Phase transition analysis DHB-AZN-n	31

List of Abbreviations

LCs	:	Liquid Crystals
R.B.	:	Round bottom flask
PXRD	:	Powder X-ray Diffraction
FTIR	:	Fourier Transform Infrared Spectroscopy
POM	:	Polarizing Optical Microscope
NMR	:	Nuclear Magnetic Resonance
DCM	:	Dichloromethane
4ABN	:	4-Aminobenzonitile
2-OHEt	:	3,5-Dihydroxybenzoate
Cry	:	Crystalline
N	:	Nematic
Sm	:	Smectic
Iso	:	Isotropic
TLC	:	Thin Layer Chromatography
UV	:	Ultraviolet
Str.	:	Stretching
LCT	:	Liquid Crystal Trimer
Ppt.	:	Precipitate
eq.	:	equivalent
DSC	:	Differential Scanning Calorimetry

Index

Abstract i

List of figures ii

List of tables iv

List of abbreviations v

Chapter 1: Introduction

1.1 Soft materials 1
1.2 LCs 2
1.3 Discovery and background of LCs 2
1.4 Classification of LCs 4
1.4.1 Thermotropic LCs 4
1.4.1.1 Calamitic LCs 4
1.4.1.2 Discotic LCs 4
1.4.1.3 Bent core LCs 4
1.4.1.4 Nematic LCs 5
1.4.1.5 Smectic LCs 5
1.4.1.6 Cholesteric (Chiral Nematic) LCs 6
1.4.1.7 Columnar (Disotic) LCs 6
1.4.2 Lyotropic LCs 7
1.4.3 Metallotropic LCs 7
1.5 Liquid crystals Trimers 7
1.5.1 Classification of liquid crystal Trimers 8
1.5.1.1 Symmetric Liquid Crystal Trimers 8
1.5.1.2 Non-symmetric Liquid Crystal Trimers 9
1.6 Azo Benzene 9
1.7 Literature survey 10
1.7.1 Azo based liquid crystal trimers 10
1.8 Characterization Techniques 11
1.8.1 Powder X-ray Diffraction (PXRD) 11
1.8.2 Fourier Transform Infrared Spectroscopy (FTIR) 12
1.8.3 Polarized Optical Microscope (POM) with Hot stage 13
1.8.4 Nuclear Magnetic Resonance (NMR) spectroscopy 14
1.8.5 UV-Vis Spectrophotometer 15

Chapter 2: Synthesis and Characterization of Azo based Trimers

2.1 Introduction 18
2.2 Materials and Methods 19
2.2.1 Materials 19
2.2.2 Instruments 20
2.2.3 Synthetic Procedures 20
2.3 Results and discussions 22
2.3.1 Characterization 22

2.3.1.1 PXRD 22
2.3.1.2 FTIR 23
2.3.1.3 NMR 24
2.3.1.4 POM with hot stage analysis 30
2.3.1.5 Photo-switching studies 31
2.4 Conclusions 33
2.5 Future Perspectives 33
2.6 References 34
2.7 Appendix 36

CHAPTER 1

INTRODUCTION

1.1 Soft materials

The propensity of soft materials to deform significantly with mild applied stresses makes them a suitable for variety of applications. Soft materials are elastic, flexible and exhibit viscoelasticity, unlike hard materials, which are usually brittle and rigid. They comprise a vast array of materials, including liquid crystals (LCs), biological tissues, gels, foams and polymers. Because of their special mechanical and physical characteristics, these materials are significantly studied in several disciplines, including biology, materials science, engineering and medicine [1].

The following is a brief description of the soft materials:

i) **Polymers:** Polymers are large molecules made up of subunits that repeat. They may be:

Thermoplastic polymer: Thermoplastics soften when heated, allowing them to be moulded and harden again upon cooling, some of the examples include polystyrene and polyethylene.

Thermosetting polymer: Thermosetting polymer undergoes permanent hardening when exposed to heat, such as epoxy resins.

Elastomers: Flexible polymers that can stretch and revert to their original form after being deformed, such as rubber and silicone.

ii) **Gels:** Gels are semi solid substances made up of a liquid-swollen network of polymers. They are used in many different fields, such as soft robotics, wound dressings, and medication delivery systems.

iii) **Foams:** Gas bubbles scattered with in a liquid or solid substrate make up foams. Applications for them include thermal insulation, cushioning, and lightweight structural elements.

iv) **Biological soft tissues:** These are naturally occurring soft materials present in living things. Because of their hierarchical structure, they display complicated behaviours and are being researched for use in bioengineering and medicine.

v) **LCs:** The substances that exhibit fluidity like liquids while maintaining a certain level of molecular organization in the melt are called LCs.

1.2 Liquid Crystals (LCs)

In between isotopic liquids and crystalline solids, there is a special state of matter known as LCs (**Fig 1.1**). The molecular arrangement resembles crystalline solids, yet they can still flow like liquids [2]. The following is an explanation of the essential properties of LCs:

i) Anisotropy: The molecular assembly in the liquid crystalline state exhibits direction dependent properties such as refractive index, birefringence, etc. which attributes to the anisotropy of LCs.

ii) Order of molecules: There is some long-range molecular order in LCs, in contrast to the repeating positional order found in crystalline solids. This arrangement is more organised than that of typical liquids but less rigid than that of crystalline solids.

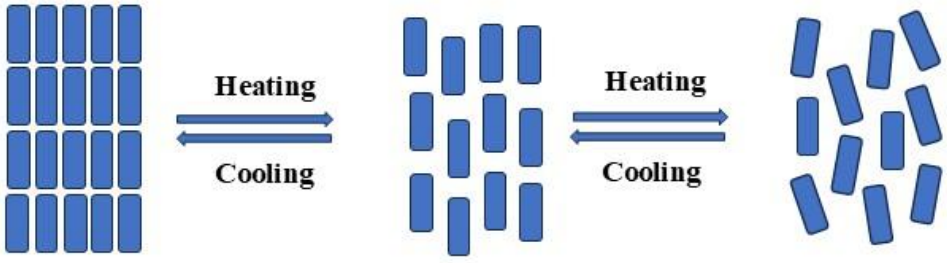


Fig 1.1 Phase transition in LCs.

1.3 Discovery and Backgrounds of LCs

With significant contributions from a number of scientists, the history of LCs dates back to the late 19th century. While studying cholesterol benzoate in 1888, Friedrich Reinitzer, an Austrian botanist, discovered LCs (**Fig:1.2**). He described the materials as an "anisotropic fluid" because of its unusual behaviour and two melting temperatures. Reinitzer's discoveries were published in an article entitled "On the Crystalline Phases of Certain Organic Compounds" [3].

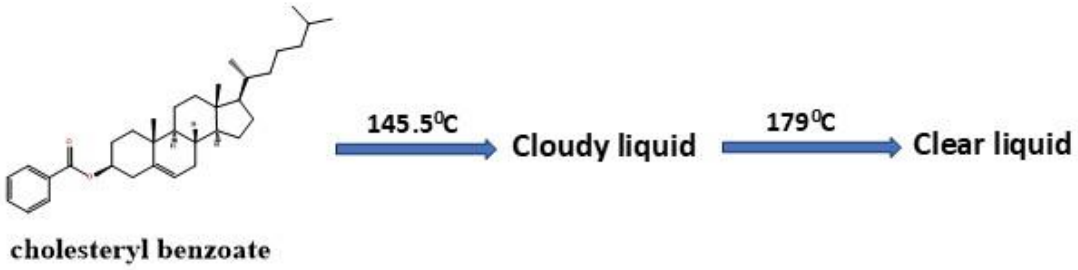


Fig 1.2 Cholesteryl benzoate (First LC).

Otto Lehmann, a German scientist, conducted extensive studies on LCs at the beginning of the twentieth century. In 1904, he coined the term "liquid crystal" and discovered a number of mesophases, such as nematic, smectic and cholesteric phases [4].

Up until the middle of the 20th century, most liquid crystal research was conducted in academia. However, during World War 2, interest in LCs grew because of the possibility of using them in the military to create display technologies for tools and weapons. George Grey and Ken Harrison, who were stationed at the University of Hull in England, achieved important breakthroughs in the 1960s. They were the first to use dynamic scattering and twisted nematic (TN) LCs to create liquid crystal displays (LCDs). Using dichroic dyes dissolved in LCs, American inventor James Fergason improved LCD technology in the 1970s with the "guest-host" display. Compared to previous LCDs, this innovation enhanced contrast and energy efficiency.

Since 1980s, LCDs, have proliferated in a wide range of electronic products, including digital watches, calculators, computers, smartphones, and televisions. New varieties of LCs and their uses, such as flexible displays, e-paper, and photonics, are being investigated in ongoing research. LCs' discovery and advancement have revolutionised display technology and sparked research in the area of photonics, optical and sensor applications.

1.4 Classification of LCs

The three primary classes of LCs are thermotropic, lyotropic, and metallotropic.

1.4.1 Thermotropic LCs

The substances that exhibit liquid crystallinity on heating and/or cooling are called thermotropic LCs [5]. Thermotropic LCs are further categorised according to their shape, which includes

1.4.1.1 Calamitic LCs

Calamitic LCs are distinguished by their elongated, rod-like structures. They are also known as rod-shaped or nematic LCs. It is common for these molecules to line up parallel to one another, creating a nematic phase. Calamitic LCs are extensively utilised in LCDs and other display technologies because of their capacity to regulate light transmission through the molecular alignment (**Fig 1.3**) [6].

1.4.1.2 Discotic LCs

Discotic LCs are distinguished by their disc-like molecular structures. Columnar formations are created when these molecules stack on top of one another. The discs in these formations have molecular planes parallel to each other and are valuable in a variety of applications, including organic semiconductors, photovoltaic devices, and sensors, due to their distinctive electrical and optical characteristics (**Fig 1.3**) [7].

1.4.1.3 Bent core LCs

In contrast to calamitic and discotic LCs, which have rod-like and disc-like structures, respectively, bent-core LCs features bent or V-shaped molecular structures. These molecules frequently create layered smectic phases when they self-assemble into distinctive shapes. Bent core LCs are being investigated for several uses, such as photonic devices and sophisticated display technologies, because of their unique structures, which also result in intriguing electro-optical properties (**Fig 1.3**) [8].

Fig 1.3 Schematic representation of Calamatic, Discotic, and Bent core LCs.

Moreover, thermotropic LCs are categorised according to the phase they exhibit as follows:

1.4.1.4 Nematic LCs

Nematic LCs lack long-range positional order and have molecules aligned parallel to one another **(Fig 1.4)**. They are potentially used in LCDs because the molecules can be aligned with the applied voltage, preserving the directional order [9].

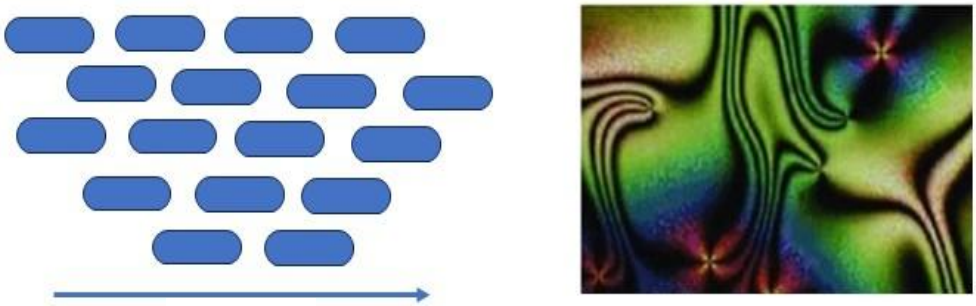


Fig 1.4 Texture of Nematic liquid crystal phase.

1.4.1.5 Smectic LCs

Smectic LCs have a layered arrangement in their liquid crystalline state, which permits molecules to move smoothly over one another [10]. These are further categorised into:

i) **Smectic A (SmA):** The molecules are oriented parallel to one another and at a right angle to the layers (**Fig 1.5**).

ii) **Smectic C (SmC):** The molecular arrangement is similar to SmA, but the molecules are inclined relative to the layer normal (**Fig 1.5**).

iii) **Smectic B (SmB)** The molecules are inclined and organised into double layers (**Fig 1.5**).

iv) **Smectic F (SmF)** With each layer, the molecules arrange themselves into a helical pattern (**Fig 1.5**).

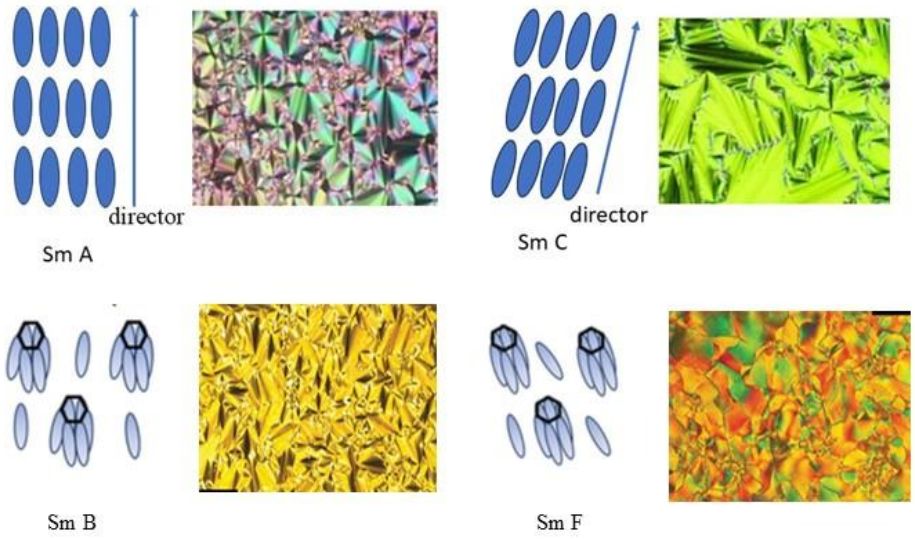


Fig 1.5 Texture of Smectic LCs phase.

1.4.1.6 Cholesteric (Chiral Nematic) LCs

These LC states exhibit light reflection and create iridescent colours as a result of their twisted helical molecular arrangement (**Fig 1.6**). They are commonly utilized in reflective displays, wave guides and security devices [11].

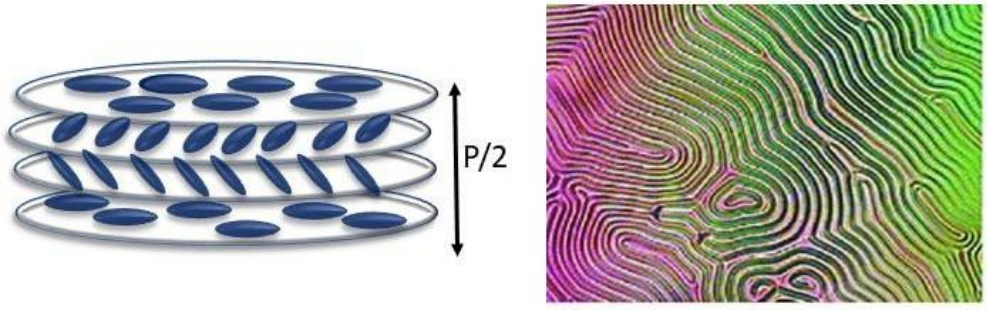


Fig 1.6 Texture of Chiral Nematic liquid crystal phase.

1.4.1.7 Columnar (Discotic) LCs

These molecules display liquid crystalline behaviour along one or two dimensions, forming columns or stacks **(Fig 1.7)**. They are employed in photonic devices and organic electronics [12].

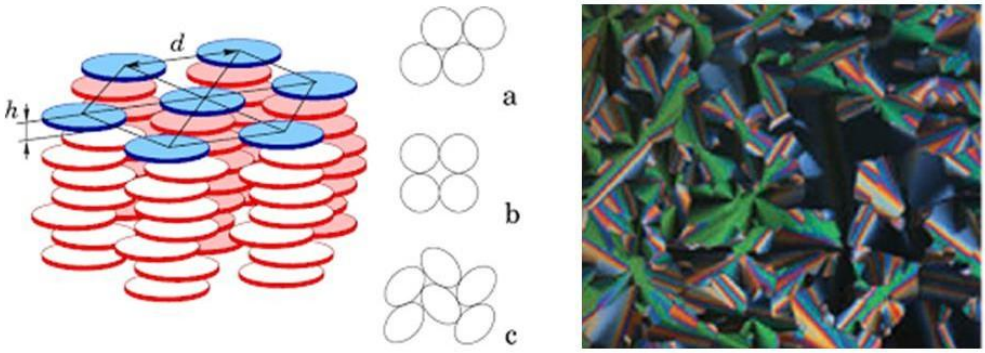


Fig 1.7 Texture of Columnar liquid crystal phase.

1.4.2 Lyotropic LCs

When amphiphilic molecules dissolve in a solvent, like water, lyotropic LCs are formed. Both hydrophilic and hydrophobic components are present in these molecules. When dissolved in a suitable solvent, the self-assembly of the molecules into organized structures forms the liquid crystalline phase. Depending on variables like molecular structure and concentration, the structure can be lamellar (layered), hexagonal, or cubic. Applications for lyotropic LCs are numerous in the field of food science, cosmetics, and medicinal chemistry [13].

1.4.3 Metallotropic LCs

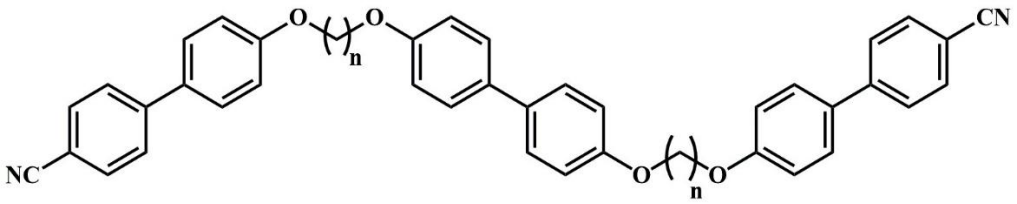
LCs that are metallotropic contain both organic and inorganic components. Temperature, concentration, and the proportion of inorganic to organic molecules affect their liquid crystal transition. The addition of long-chain soap-like molecules results in a series of discrete phases, each with a unique liquid crystalline behaviour that varies according to temperature and the ratio of inorganic to organic composition [14].

Out of the above classification, there is a special class of thermotropic LCs known as liquid crystal trimers.

1.5 Liquid Crystal Trimers (LCTs)

The origin of liquid crystal trimers can be traced back to the early investigations of liquid crystal oligomers, especially dimers, which were initially explored in the

1980s as analogues for semi-flexible main-chain LCT [15]. This foundation work paved the way for the synthesis and study of the first liquid crystal trimers in the late 1990s, notably including molecules like 4,4'-bis[4-(cyanobiphenyl-4-yloxy)alkoxy]biphenyls **(Fig 1.8)** [16]. These compounds revealed distinct mesophase characteristics, strongest odd-even effects in phase transition behaviour, emphasizing the significant role of molecular design in determining their liquid crystalline properties [17].



n = 4-11

Fig 1.8 First investigated LCT.

LCTs are a type of oligomer consisting of three mesogenic units linked by flexible spacers. This structural design serves as an intermediate between single-unit LCs and long-chain polymers, enabling the manifestation of distinctive mesophases and physical characteristics. Exploring these oligomeric systems enhances our understanding of how molecular structure influences the liquid crystalline behaviour, which is essential for the innovation of high-performance functional materials [18].

1.5.1 Classification of LCTs

Based on the structural organization of their mesogenic components, liquid crystal trimers are generally categorized as either symmetric or non-symmetric.

1.5.1.1 Symmetric LCTs

Symmetric LCT consist of three mesogenic segments arranged linearly with structural uniformity, typically linked by identical flexible spacers. The presence of molecular symmetry enables consistent intermolecular interactions, which facilitates the formation of higher ordered mesophases such as nematic, smectic A,

and twist-bend nematic phases. Due to their reliable and well-defined phase behaviour, symmetric trimers are considered ideal for use in display systems and other technologies that depend on controlled liquid crystalline characteristics [19, 20].

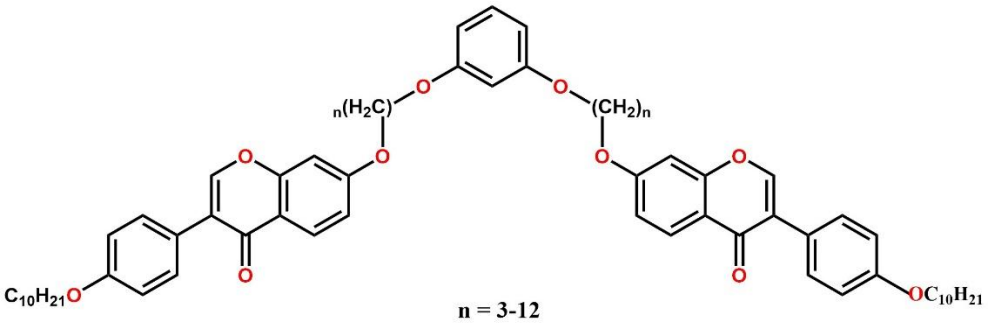


Fig 1.9 Symmetric LCT.

1.5.1.2 Non-symmetric LCTs

Non-symmetric LCTs feature varied mesogenic groups or uneven spacer lengths, resulting in molecular asymmetry that often gives rise to more intricate or less conventional mesophases. This lack of symmetry can lead to the emergence of uncommon phase behaviors, including twist-bend nematic and other modulated structures. Such characteristics make these trimers especially valuable for the development of functional materials with adjustable optical and electro-optical properties. The overall performance of these systems is strongly influenced by the combination of asymmetry, spacer dynamics, and mesogen composition. Owing to their wide-ranging mesomorphic behaviors, non-symmetric trimers are ideal for advanced applications where specialized liquid crystal properties are required, such as in smart materials and high-performance photonic devices [21].

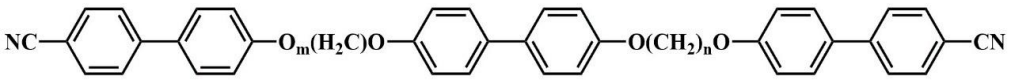


Fig 1.10 Non-symmetric LCT.

1.6 Azobenzene

Azobenzene is an organic compound which comprises of two benzene rings that are connected by a nitrogen-nitrogen double bond (-N=N-), referred as an azo

linkage. It exists as two geometrical isomers, *trans* form and *cis* form. Upon irradiation of UV light, the trans form can switch to *cis* form. Again, the back relaxation of the *cis* form to *trans* form can take place by exposing them to visible light radiation or by keeping in dark condition (**Fig 1.11)**. This unique light-responsive behaviour makes azobenzene highly valuable in the field of photo-responsive materials, such as photo switches, photochromic lenses, and optical data storage devices [22].

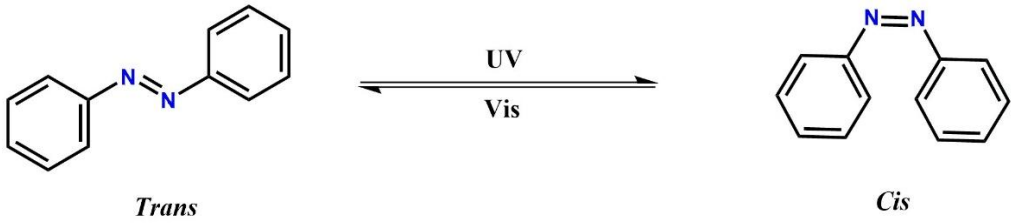


Fig 1.11 Photo-isomerization process in azobenzene.

1.7 Literature Survey

1.7.1 Azo Based LCTs

Azo based LCT represent a distinct category of oligomeric compounds that feature azo (-N=N-) linkage either embedded within or connecting their mesogenic segments. These materials uniquely integrate the directional properties of LCs with the light-responsive nature of azo functionalities, making them ideal candidates for application in cutting-edge photonic and optical technologies. The azo group plays a dual role; its rigid and planar structure supports liquid crystalline behavior, while its ability to undergo reversible *trans-cis* photoisomerization upon light exposure enables tunable control over molecular orientation and phase transitions. In trimeric systems, azo units may be positioned in the central core, on the terminal mesogens, or within the flexible spacers, each affecting the resulting mesophase, often leading to nematic, smectic, or even twist-bend nematic structures, depending on molecular symmetry and spacer length. Due to these dynamic properties, azo-based trimers show promising applications in light-sensitive actuators, reconfigurable optical devices, and data storage systems [23-25]. Further, incorporating these terminal groups alters the dipole moment of the trimers, which in turn affects their liquid crystalline behaviour. In this context, current study

focuses on the synthesis of azo-based trimers of Ethyl 3,5-bis(4-(4-((*E*)-(4-cyanophenyl)diazenyl)phenoxy)alkoxy)benzoate.

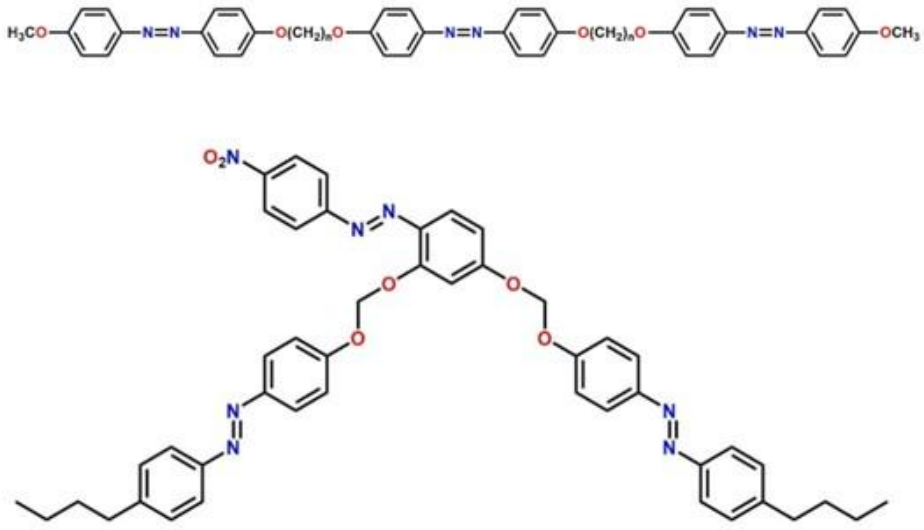


Fig 1.12 Some of the azo based LCTs reported in the literature.

1.8 Characterization Techniques

1.8.1 Powder X-ray Diffraction (PXRD)

PXRD is used to examine the composition and crystalline structure of materials. X-rays are often released from metal-based sources, such as Cu, Mo, or Ag, which are generated when fast-moving electrons collide with these metal targets. Diffraction patterns are produced when these X-rays are diffracted from the crystalline or amorphous materials **(Fig 1.13)**. Properties like phase purity and the material's inherent qualities are then evaluated by closely examining these patterns. The nature of the diffraction patterns depend on the internal atomic structure of the materials. This phenomenon is explained by Bragg's law of diffraction [26].

Bragg's law of diffraction is expressed as:

$2d \sin \theta = n \lambda$

Where:

d = interplanar spacing

λ = wavelength of irradiated X-ray

θ = angle at which the X-ray strikes the crystal planes

n = order of the reflected wave

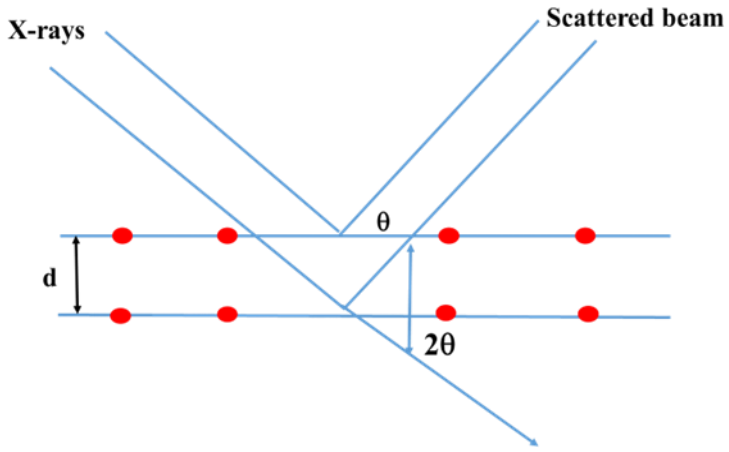


Fig 1.13 X-ray diffraction phenomena of a crystalline substance.

Specialized X-ray diffractometers, which consist of an X-ray source, a sample holder made for powdered materials, and a detector to catch the diffracted X-rays, are frequently used in PXRD research.

Fig 1.14 Powder X-ray Diffractometer.

1.8.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is a commonly used analytical tool to analyze organic compounds. FTIR spectroscopy **(Fig 1.15)** records the absorbance or transmittance spectrum that results from passing infrared light through a material. The foundation of FTIR spectroscopy is the idea that certain chemical bonds absorb infrared light at particular frequencies, producing unique peaks in the spectrum. Researchers can identify functional groups, ascertain molecular conformations, and evaluate the sample's composition by examining the positions and intensities of these peaks [27].

Fig 1.15 FTIR spectrophotometer.

1.8.3 Polarized Optical Microscopy (POM) with hot stage

Employing a polarized Optical Microscope (POM) equipped with a hot stage (as shown in **Fig 1.16**) provides a comprehensive and methodical way to investigate the LCs. This technique is particularly useful for examining their distinct optical textures and monitoring the phase transition temperatures [28].

Equipment and Setup

Hot Stage: A device with accurate temperature regulation used to heat or cool samples, facilitating the observation of thermal phase transitions in liquid crystal materials.

Sample Preparation Tools: This includes glass slides, cover slips, and preparation of thin liquid crystal specimens.

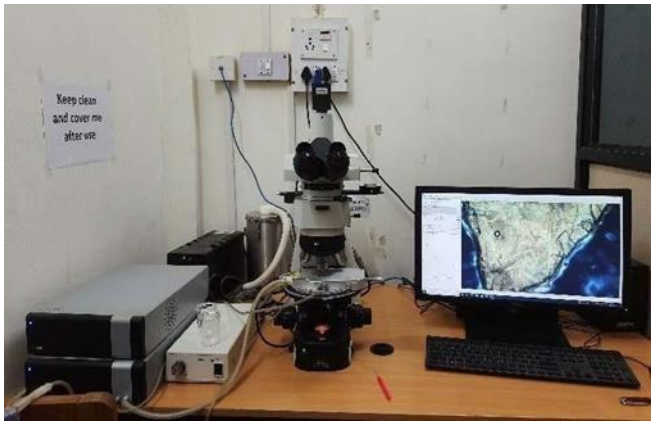


Fig 1.16 POM Instrument equipped with a Hot stage.

1.8.4 Nuclear Magnetic Resonance (NMR) Spectroscopy

A potent analytical method for figuring out the structure, dynamics, reaction state, and chemical environment of molecules is nuclear magnetic resonance (NMR) spectroscopy **(Fig 1.17)**

Essential Components of an NMR Spectrometer

Magnet: Produces a strong and uniform magnetic field, often using a superconducting system.

Radiofrequency Transmitter: Emits radio wave pulses to stimulate the nuclei within the sample.

Receiver: Typically, a slender glass tube that contains the sample being analyzed.

Computer: Analyzes the received signals and generates the corresponding NMR spectrum.

Fig 1.17 NMR Instrument.

Different Types of NMR Spectroscopy

Proton NMR (^{1}H NMR): The most widely used type of NMR, it analyses hydrogen atoms within a molecule. It reveals details about the quantity, types, and chemical environments of hydrogen atoms.

Carbon-13 NMR (^{13}C NMR): Focuses on examining carbon atoms with different chemical environment in a compound. Although the abundance of ^{13}C nuclei is less than ^{1}H nuclei, it offers valuable insight into the carbon framework of the organic molecules.

Multinuclear NMR: Expands NMR analysis to other nuclei such as phosphorus-31 (^{31}P), fluorine-19 (^{19}F), and nitrogen-15 (^{15}N), enhancing the understanding of molecular structure.

Two-Dimensional NMR (2D NMR): Methods such as COSY, HSQC, and NOESY enable the correlation of signals from various nuclei, providing in-depth structural and interactional information about molecules**.**

1.8.5 UV-Vis Spectrophotometer

UV-Vis spectrophotometer works on the principle of Beer-Lamberts Law which states that the absorbance of a solution is directly proportional to the concentration of the absorbing species, the path length of the sample cell, and the molar absorptivity of the substance at a particular wavelength. Certain molecules having π or non-bonding (n) electrons, can absorb the ultraviolet or visible light that causes an excitation from higher occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO). UV-vis spectroscopy assesses how much light passes through a sample (I) compared to the incident light (I_O).

$$\mathbf{A = \varepsilon\, c\, l}$$

Where:

A = absorbance (unitless)
ε = molar absorptivity or extinction coefficient (L mol^{-1} cm^{-1})
c = concentration of the solution (mol L^{-1})
l = path length of the light through the solution (cm)

Fig 1.18 UV-Vis Instrument.

CHAPTER 2

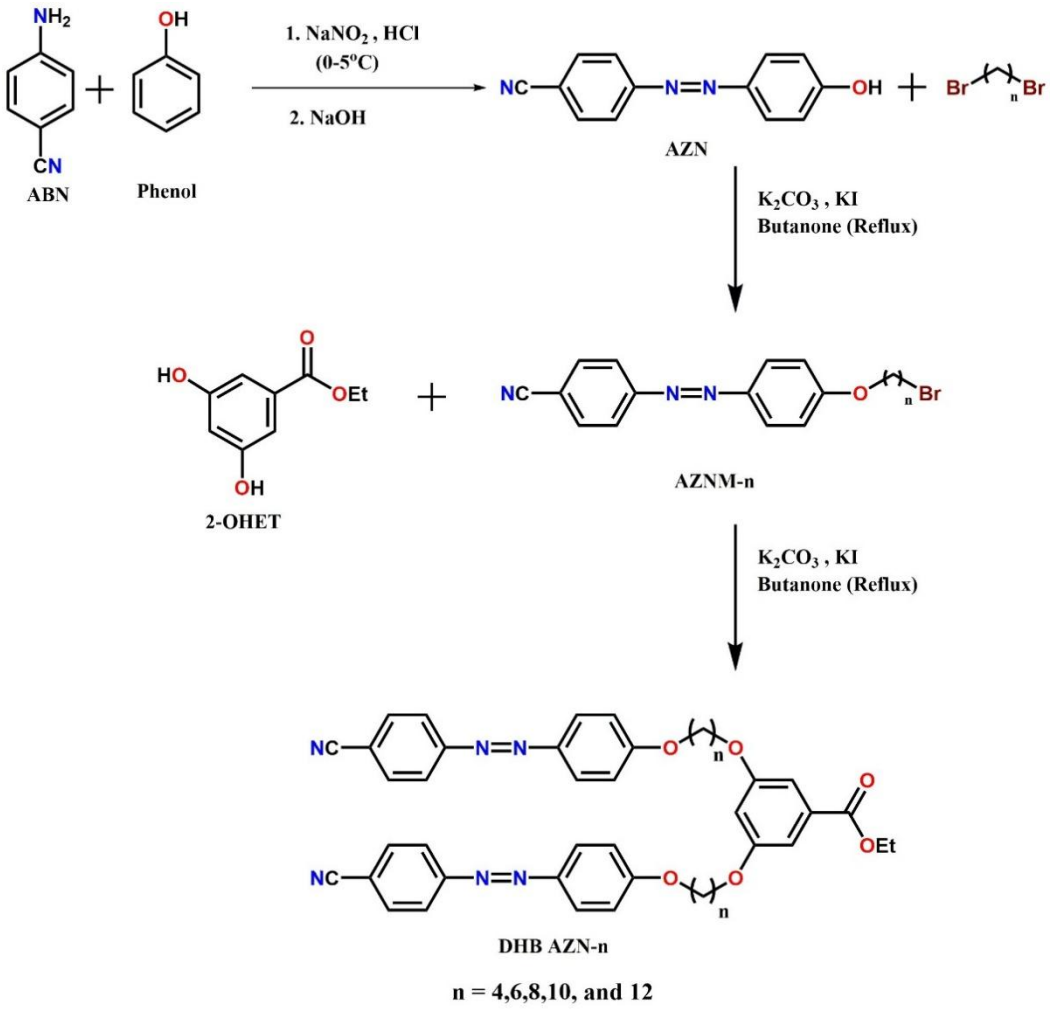
SYNTHESIS AND CHARACTERIZATION OF Ethyl 3,5-bis(4-(4-((*E*)-(4-cyanophenyl) diazenyl)phenoxy)alkoxy)benzoate Trimers

---

2.1 Introduction

The ability of photo-switchable LC materials to reversibly change their mesophase characteristics and molecular ordering in response to light has drawn interest. They greatly improve this light-sensitive behaviour by adding azo benzene (N=N) units to their chemical structure. In the literature survey, we already studied that almost all trimers that have been synthesized, contain azo benzene as a central or terminal unit with ester and nitrile as terminal groups and they exhibited improved LC characteristics.

In order to induce photo-switchable features, we have focused on synthesising azo based liquid crystal trimers. This could lead to new technological applications by enabling dynamic material properties and functions. Three step reaction was carried out to synthesize the target molecules (DHB-AZN-n). The first step involved diazotization of 4-aminobenzonitrile to form diazonium salt that further undergoes diazo coupling with phenol to form an azo compound. In the second step, the azo compound undergoes O-alkylation by reacting with 1,n-dibromoalkane (n = 4, 6, 8, 10, 12) to form alkylated azo benzene (AZNM-n). Further, the reaction of ethyl-3,5-dihydroxybenzoate (2-OHET) with AZNM-n was performed to obtain the azo based trimers, Ethyl 3,5-bis(4-(4-((E)-(4-cyanophenyl) diazenyl)phenoxy)alkoxy)benzoate (DHB-AZN-n) **(Scheme 2.1)**.



Scheme 2.1 Synthesis of azo-based trimer molecules (DHB-AZN-n).

2.2 Materials and Methods

2.2.1 Materials

Analytical-grade reagents such as NaOH, HCl, K_2CO3, KI were used in the synthesis of target compounds. High putity solvents, such as butanone, petroleum ether, ethanol, DCM (dichloromethane), and ethyl acetate (EtOAc), were used without further purification. Dibromo alkanes from Sigma-Aldrich, ethyl-3,5-dihydroxybenzoate, phenol and 4-aminobenzonitrile from TCI, all of which were 98% pure, were among the raw materials used in the synthesis. Silica gel TLC plates of 0.25 mm 60F254 grade were used to monitor the reaction. Column chromatography using silica gel of 100-200 mesh size was used along with ethyl acetate - petroleum ether (60-80) solvent system as the mobile phase to purify the crude products.

2.2.2 Instruments

TLC plates were visualised using a UV chamber from Bio Technics India (BTI) comprising both short-wave (254 nm) and long wave (365 nm) UV light. A Bruker D8 Advance Eco X-ray diffractometer fitted with a silicon sample holder unit was used to perform the PXRD (Powder X-ray Diffraction) investigation. A Shimadzu IR affinity spectrometer was used to collect FTIR spectra to determine the functional groups in the synthesized compounds and provide preliminary confirmation. The structural integrity and purity of the synthesized compounds were confirmed using ^{1}H and ^{13}C NMR spectroscopy, operating at 500 MHz. A Nikon POM (Polarized Optical Microscope) equipped with a Linkam Hot Stage LTS 420 was used to analyse the mesophase. Heating cycles from room temperature to 180 ^{o}C and cooling cycles from 180 ^{o}C to 33 ^{o}C at a rate of 5 ^{o}C per minute were performed twice to identify the texture of the mesophases. Further, the photo-switching behavior of the compounds to 365 nm UV light (1 W) in solution state was analyzed utilizing a Shimadzu 1800 UV-Vis spectrophotometer.

2.2.3 Synthetic procedure

i) Synthesis of (*E*)-4-((4-hydroxyphenyl)diazenyl)benzonitrile

A solution of 4-aminobenzonitrile (4-ABN, 0.035 moles) was prepared by dissolving it in a mixture of 8 ml of concentrated hydrochloric acid and 8 ml of water. The solution was kept at a temperature between 0-5 ^{o}C using an ice bath. After that, 0.0351 moles of sodium nitrite ($NaNO_2$) dissolved in 10 ml of water was added, and the mixture was stirred at 0-5 ^{o}C for two hours resulting in the diazonium salt. Meanwhile, 3.2 ml of phenol (0.0355 moles) in 22.5 ml of 10% sodium hydroxide (NaOH) solution was prepared and the diazonium salt solution was added gradually to it while stirring continuously for another one hour at 0-5 ^{o}C. To adjust the pH, hydrochloric acid was added to the reaction mixture. As a result, an orange-colored azo compound was precipitated. The product was filtered, washed with water, and dried overnight in a vacuum oven at 90 ^{o}C (yield = 96.77 %).

ii) Synthesis of (*E*)-4-((4-((n-bromoalkyl)oxy)phenyl)diazenyl)benzonitrile

In a round bottom flask (R.B.), AZN (1 eq.) was combined with K_2CO_3 (3 eq.) and a catalytic amount of KI. The mixture was dissolved in 15-20 ml of butanone and stirred

continuously at a temperature of 70-80 ºC for about 15 minutes. Subsequently, 1,n-dibromoalkane (3 eq.) with varying spacer chain length (n = 4, 6, 8, 10 and 12), was gradually added while maintaining a warm reaction environment. The reaction was then refluxed at 70-80 ºC for 22 hours and then filtered. The solvent was then evaporated under vacuum, resulting in orange solid, which was then purified through column chromatography using a mobile phase of ethyl acetate and petroleum ether in 8 % v/v ratio.

Table 2.1 The yield of the products (AZNM-n)

Compound name	**Yield %**
AZNM-4	60.17
AZNM-6	58.03
AZNM-8	55.65
AZNM-10	61.35
AZNM-12	57.80

iii) Synthesis of Ethyl 3,5-bis(4-(4-((*E*)-(4-cyanophenyl)diazenyl)phenoxy)alkoxy)benzoate Trimers

In a round bottom flask, 2-OHET (1 eq.), K_2CO_3 (4 eq.) and a catalytic amount of KI was taken. The mixture was dissolved in 15-20 ml of butanone and stirred continuously at a temperature of 70-80 ºC for about 20 minutes. Subsequently, 3 eq. of AZNM-n in butanone (n = 4, 6, 8, 10 and 12) was gradually added in warm conditions. The reaction mixture was then refluxed at 70-80 ºC for 22 hours followed by filtration and solvent evaporation under reduced pressure. The resulting orange-colored solid product was purified through column chromatography using a mobile phase of ethyl acetate and petroleum ether in 16 % v/v ratio.

Table 2.2 The yield of the products (DHB-AZN-n)

Compound name	Yield %
DHB-AZN-4	44.08
DHB-AZN-6	45.12
DHB-AZN-8	43.06
DHB-AZN-10	46.82
DHB-AZN-12	42.79

2.3 Results and Discussion

2.3.1 Characterization

A variety of analytical techniques, including PXRD, FTIR, ^{1}H NMR, ^{13}C NMR, POM with hot stage, UV-Vis spectroscopy, were employed to analyze the intermediates as well as the LCTs, DHB-AZN-n.

2.3.1.1 PXRD

The PXRD patterns of DHB-AZN-n (n = 4, 6, 8, 10, and 12) show a clear distinction from those of the starting materials, providing initial evidence for the successful formation of the target compounds (**Fig 2.2, and Fig A1-4**).

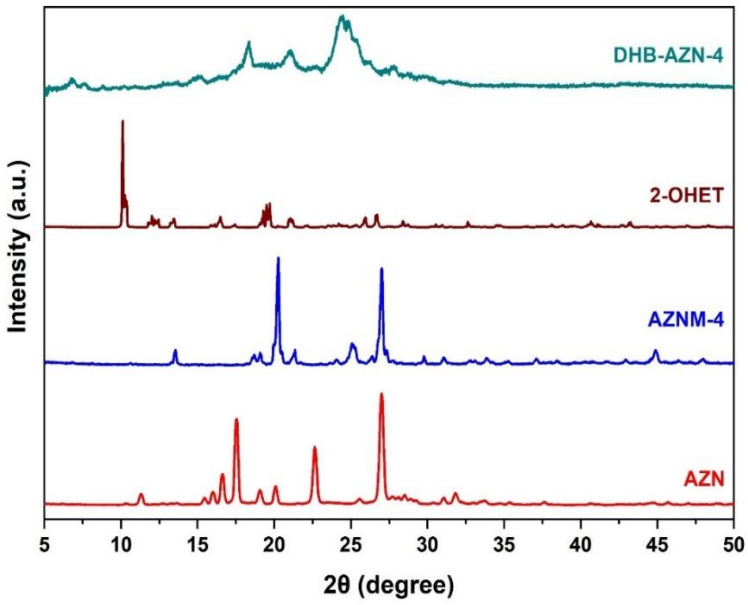


Fig 2.2 PXRD pattern DHB-AZN-4.

2.3.1.2 FTIR

The FTIR spectra revealed the absence of the OH stretching vibration in both AZNM-n and DHB-AZN-n (n = 4, 6, 8, 10, and 12). In the case of DHB-AZN-n, the appearance of characteristic absorptions for sp^3 C-H stretching, CN stretching and C=O stretching confirmed the synthesis of the DHB-AZN-n compounds (**Table 2.3-2.4 and Fig 2.3, and A5-8**).

Table 2.3 FTIR data of AZNM-n

Compound name	**sp^3 CH str. (cm^{-1})**	**CN str. (cm^{-1})**
AZNM-4	2952, 2883	2219
AZNM-6	2945, 2550	2221
AZNM-8	2927, 2850	2220
AZNM-10	2919, 2851	2225
AZNM-12	2921, 2850	2226

Table 2.4 FTIR data of DHB-AZN-n

Compound name	**sp^3 CH str. (cm^{-1})**	**CN str. (cm^{-1})**	**CO str. (cm^{-1})**
DHB-AZN-4	2937, 2863	2227	1715
DHB-AZN-6	2942,2871	2226	1719
DHB-AZN-8	2921, 2854	2226	1709
DHB-AZN-10	2926, 2848	2221	1717
DHB-AZN-12	2921, 2850	2218	1718

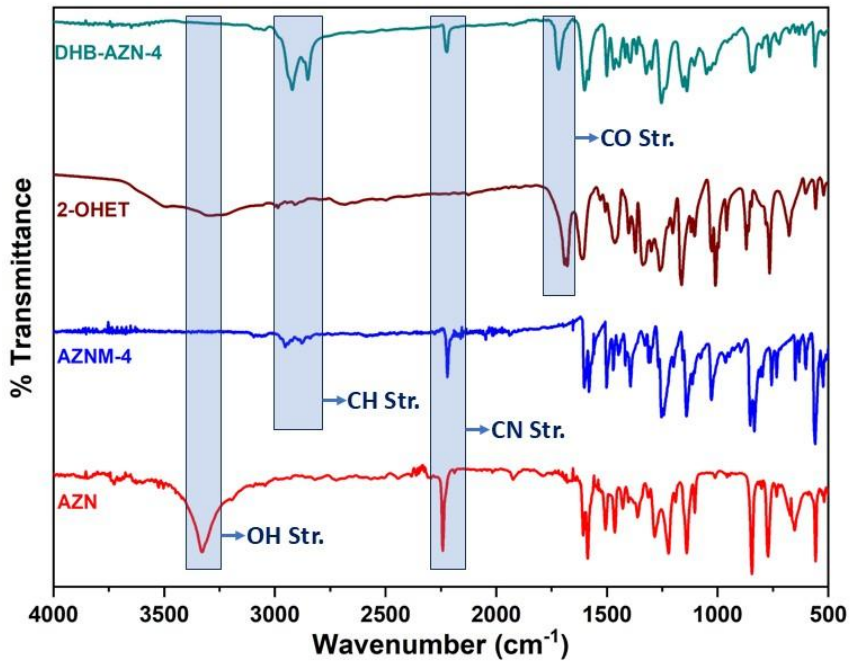


Fig 2.3 FTIR spectra of AZNM-4.

2.3.1.3 NMR

AZNM-4

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (dd, *J* = 8.8, 2.7 Hz, 4H, Ar-H), 7.80 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.03 (d, *J* = 9.0 Hz, 2H, Ar-H), 4.12 (t, *J* = 6.0 Hz, 2H, -OCH_2), 3.53 (t, *J* = 6.5 Hz, 2H, -CH_2Br), 2.10 (m, 4H, -CH_2).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.06,154,32,146.68,132.58,125.22,123.30, 118.46, 114.68, 112.77,66.93,33.66,29.18,27.87.

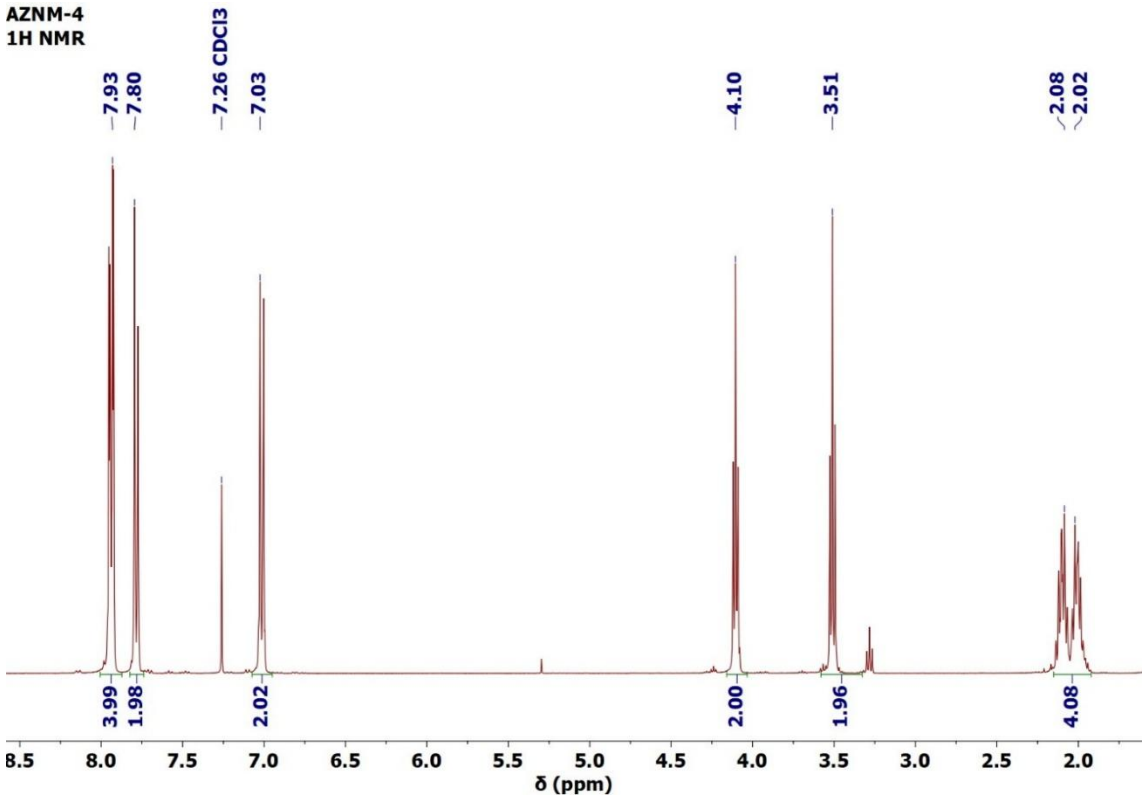


Fig 2.4 ^{1}H NMR spectra of AZNM-4.

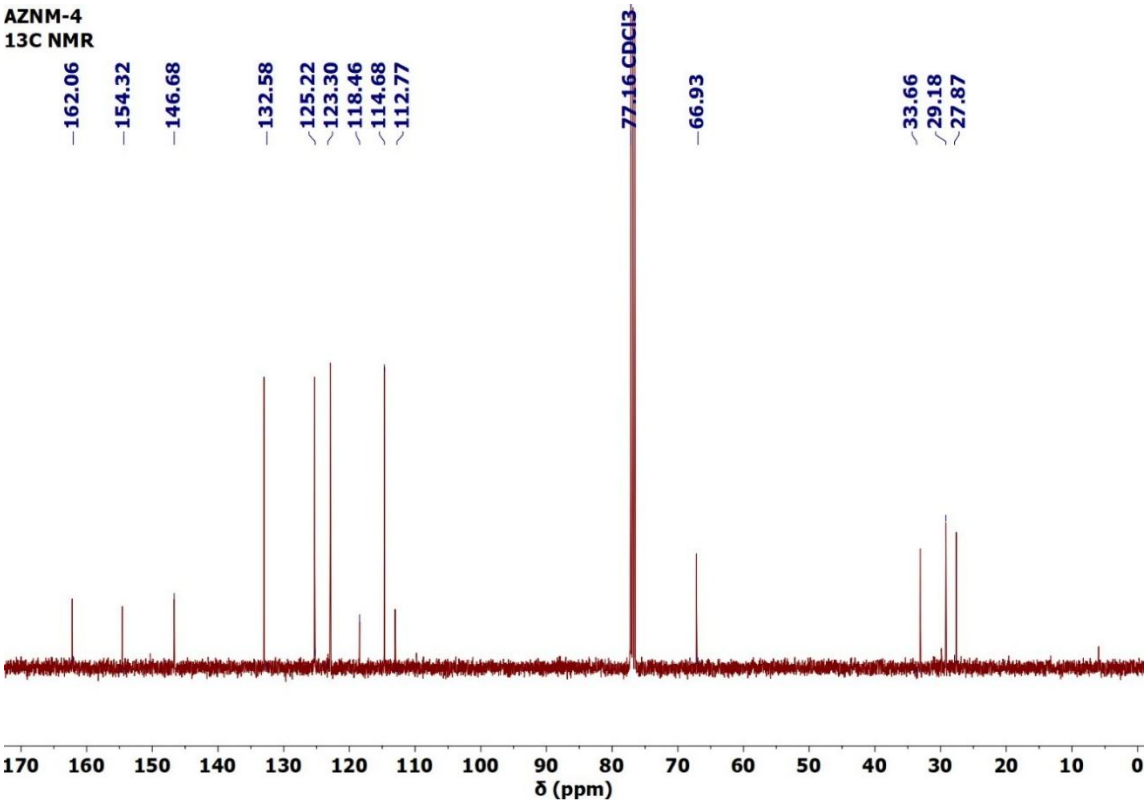


Fig 2.5 ^{13}C NMR spectra of AZNM-4.

AZNM-6

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (dd, *J* = 8.9, 2.4 Hz, 4H, Ar-H), 7.78 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.01 (d, *J* = 9.0 Hz, 2H, Ar-H), 4.07 (t, *J* = 6.4 Hz, 2H, -OCH_2), 3.44 (t, *J* = 6.7 Hz, 2H, -CH_2Br), 1.88 (d, *J* = 24.7 Hz, 4H, -CH_2), 1.54 (m, 4H, -CH_2).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.09, 125.93, 123.53, 119.11, 115.33, 113.61, 68.66, 29.42, 28.34, 25.71.

AZNM-8

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 1.9 Hz, 2H, Ar-H), 7.95 (d, *J* = 1.6 Hz, 2H Ar-H), 7.81 (d, *J* = 8.7 Hz, 2H Ar-H), 7.04 (d, *J* = 9.0 Hz, 2H , Ar-H), 4.08 (t, *J* = 6.5 Hz, 2H, -OCH_2), 3.44 (t, *J* = 6.8 Hz, 2H, -CH_2Br), 1.88 (s, 4H, -CH2), 1.46 (m, *J* = 35.3 Hz, 8H,-CH_2).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.73, 154.83, 146.74, 133.17, 125.48, 123.08, 118.68, 114.90, 113.16, 68.42, 33.96, 32.77, 29.16, 29.10, 28.68, 28.08, 25.92.

AZNM-10

^{13}C NMR (101 MHz, Chloroform-*d*) δ 133.31, 125.62, 123.22, 118.81, 115.04, 113.29, 68.62, 34.15, 32.96, 29.44, 28.88, 28.29, 26.12.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (dd, *J* = 8.8, 1.4 Hz, 4H, Ar-H), 7.79 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.02 (d, *J* = 9.0 Hz, 2H, Ar-H), 4.06 (t, *J* = 6.5 Hz, 2H, -OCH_2), 3.41 (t, *J* = 6.9 Hz, 2H, -CH_2Br), 1.85 (d, *J* = 7.6 Hz, 4H, -CH_2), 1.40 (M, *J* = 65.9 Hz, 12H, -CH_2).

AZNM-12

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 (dd, *J* = 8.9, 3.0 Hz, 4H, Ar-H), 7.78 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.02 (d, *J* = 9.0 Hz, 2H, Ar-H), 4.06 (t, *J* = 6.6 Hz, 2H, -OCH_2), 3.97 (t, *J* = 6.5 Hz, 2H, -CH_2Br), 1.80 (m, *J* = 25.8 Hz, 4H, -CH_2), 1.39 – 1.27 (m, 16H, -CH_2).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.97, 155.00, 146.89, 133.35, 125.67, 123.26, 118.87, 115.08, 113.31, 68.70, 29.75, 29.56, 29.39, 29.34, 26.22.

The NMR spectra of the compounds AZNM-n (n = 6, 8, 10, and 12) is presented in appendix. **Fig A9-16**

DHB-AZN-4

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 12.2 Hz, 8H Ar-H), 7.79 (d, *J* = 8.7 Hz, 4H, Ar-H), 7.20 (d, *J* = 2.3 Hz, 2H, Ar-H), 7.02 (d, *J* = 9.0 Hz, 4H, Ar-H), 6.64 (s, 1H Ar-H), 4.36 (m, 2H, -OCH_2), 4.14 (t, *J* = 5.6 Hz, 4H, -OCH_2), 4.08 (t, *J* = 4.9 Hz, 4H, -OCH_2), 2.02 (m, 8H, -CH_2), 1.39 (t, *J* = 5.8 Hz, 3H, -CH_3).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.72, 160.14, 147.00, 133.38, 125.69, 123.29, 118.85, 115.09, 107.87, 106.62, 67.91, 61.42, 26.13, 14.54.

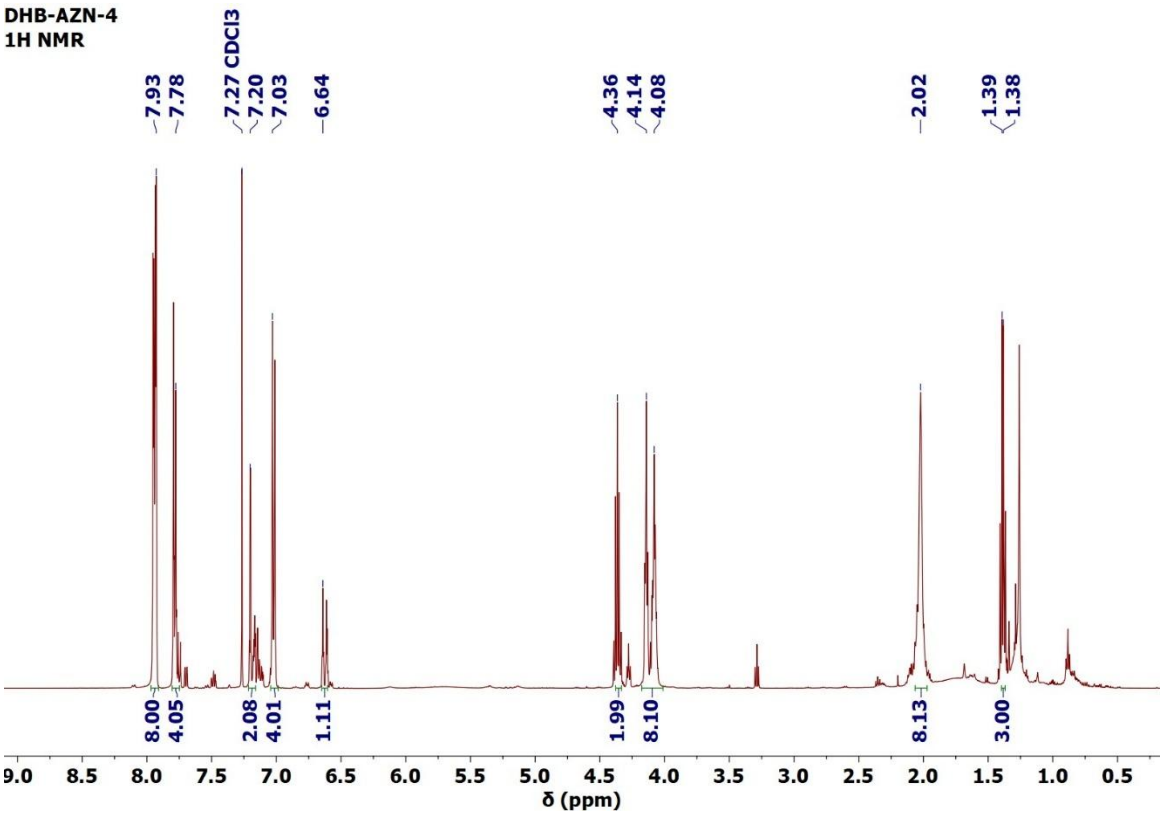


Fig 2.6 ^{1}H NMR spectra of DHB-AZN-4.

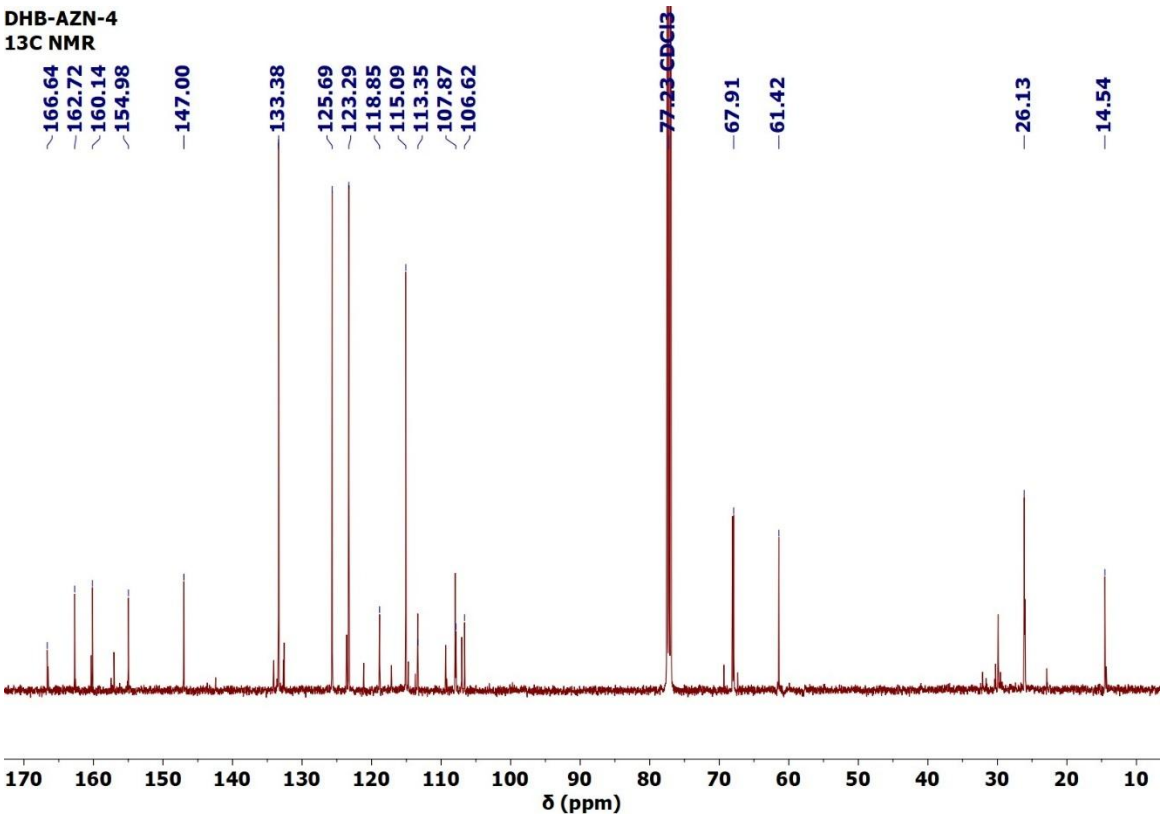


Fig 2.7 ^{13}C NMR spectra of DHB-AZN-4.

DHB-AZN-6

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 6.4 Hz, 8H, Ar-H), 7.79 (d, *J* = 8.7 Hz, 4H, Ar-H), 7.18 (d, *J* = 2.3 Hz, 2H, Ar-H), 7.02 (d, *J* = 9.0 Hz, 4H, Ar-H), 6.64 (s, 1H, Ar-H), 4.36 (m, 2H, -OCH_2), 4.08 (t, *J* = 6.4 Hz, 4H, -OCH_2), 4.01 (t, *J* = 6.4 Hz, 4H, -OCH_2), 1.84 (m, 8H, -CH_2), 1.57 (m, 8H, -CH_2), 1.39 (t, *J* = 7.1 Hz, 3H, -CH_3).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.88, 160.27, 155.00, 146.94, 133.37, 125.69, 123.28, 118.87, 113.35, 107.86, 106.56, 68.29, 61.34, 29.32, 26.05, 14.54.

DHB-AZN-8

^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.94, 160.31, 155.02, 146.91, 125.68, 123.28, 118.87, 115.09, 113.32, 107.84, 68.44, 29.46, 26.14, 14.50.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 9.1 Hz, 8H, Ar-H), 7.79 (d, *J* = 8.3 Hz, 4H, Ar-H), 7.17 (d, *J* = 2.3 Hz, 2H, Ar-H), 7.02 (d, *J* = 9.0 Hz, 4H, Ar-H), 6.64 (s, 1H, Ar-

H), 4.36 (m, 2H, - OCH_2), 4.06 (t, *J* = 6.5 Hz, 4H, -OCH_2), 3.98 (t, *J* = 5.3 Hz, 4H, -OCH_2), 1.82 (m, 8H, -CH_2), 1.34-1.5 (m, 19H, -CH_2, -CH_3).

DHB-AZN-10

^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.95, 160.31, 154.99, 146.88, 133.34, 125.66, 123.26, 118.86, 115.08, 113.30, 107.81, 106.52, 68.47, 61.28, 29.66, 26.17.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 12.5 Hz, 8H, Ar-H), 7.78 (d, *J* = 8.7 Hz, 4H, Ar-H), 7.17 (d, *J* = 2.3 Hz, 2H, Ar-H), 7.02 (d, *J* = 9.0 Hz, 4H, Ar-H), 6.63 (s, 1H, Ar-H), 4.35 (m, 2H, -OCH_2), 4.05 (t, *J* = 6.5 Hz, 4H, -OCH_2), 3.97 (t, *J* = 6.5 Hz, 4H, -OCH_2), 1.81 (m, 8H, -CH_2), 1.38 (m, 27H, -CH_2, -CH_3).

DHB-AZN-12

^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.98, 155.03, 133.37, 125.68, 123.28, 118.88, 115.10, 113.33, 68.71, 33.76, 29.72, 26.20.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 7.6 Hz, 4H, Ar-H), 7.75 (d, *J* = 7.6 Hz, 4H, Ar-H), 7.68 (d, *J* = 7.5 Hz, 4H, Ar-H), 7.28 (d, *J* = 1.5 Hz, 2H, Ar-H), 7.04 (d, *J* = 7.6 Hz, 4H, Ar-H), 6.59 (s, 1H, Ar-H), 4.34 (m, 2H, -OCH_2), 4.05 (d, *J* = 7.2 Hz, 4H, -OCH_2), 4.02 (d, *J* = 7.1 Hz, 4H, -OCH_2), 1.76 (m, 8H, -CH_2), 1.35-1.45 (m, 12H, -CH_2, -CH_3), 1.24 (m, 24H, -CH_2).

The NMR spectra of the compounds DHB-AZN-n (n = 6, 8, 10, and 12) is presented in appendix (**Fig A17-24**).

2.3.1.4 POM with hot stage analysis

The mesomorphic properties of the synthesized compound, DHB-AZN-n (n = 4, 6, 8, 10 and 12) have been analyzed utilizing a Polarizing Optical Microscope equipped with a hot stage. For all the derivatives (n = 4, 6, 8, 10 and 12) the monotropic nematogenic behaviour was observed in the cooling cycle. Additionally, decoxy (n =10), and dodecoxy (n = 12) derivatives exhibited smectic A liquid crystalline phase in the cooling cycle due to the layered arrangement of the molecules with elongated alkoxy spacers. The phase transition temperature is summarized in **Table 2.5** and the optical texture is illustrated in **Fig 2.8**.

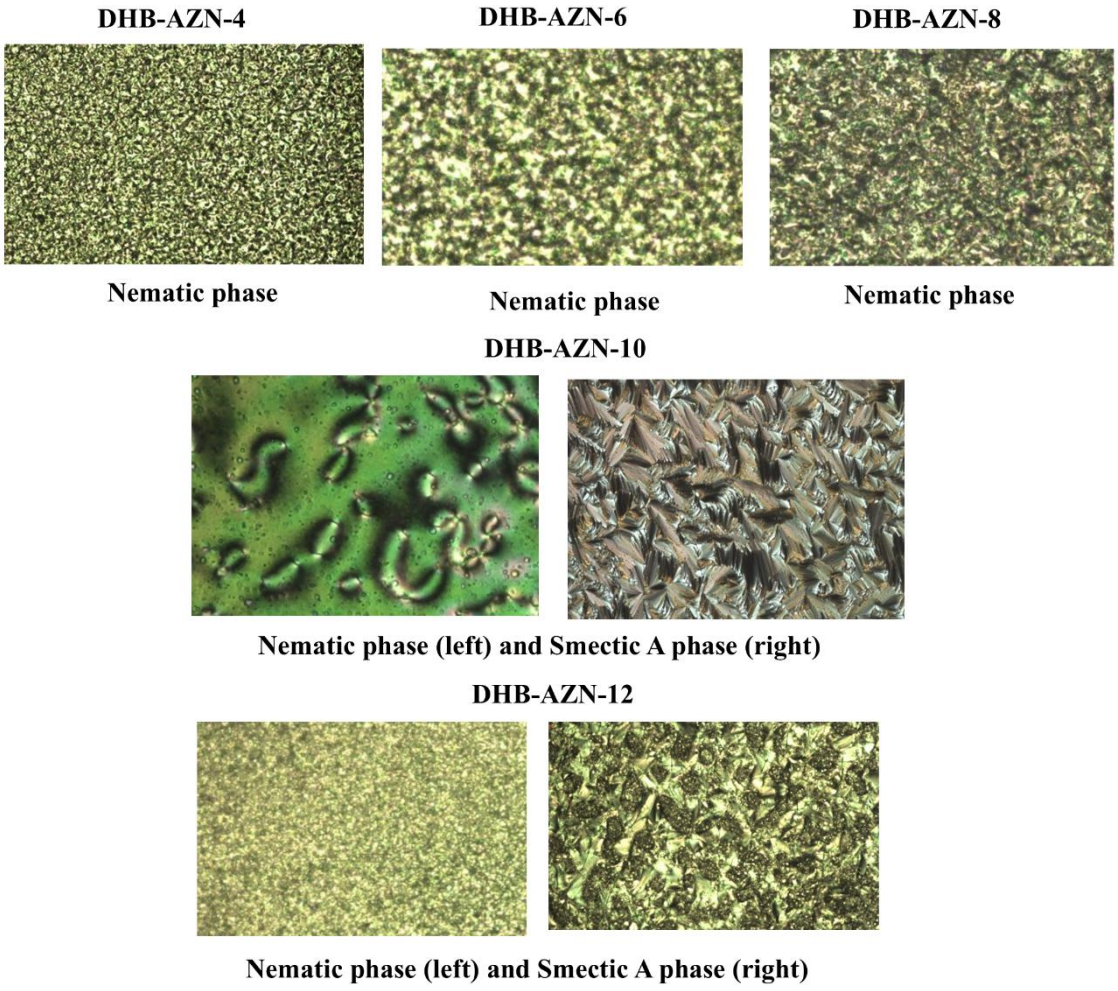


Fig 2.8 POM textures of DHB-AZN-n (n = 4, 6, 8, 10 and 12) observed in the cooling cycle.

Table 2.5 Phase transition analysis of DHB-AZN-n

Compound code	Phase transition (POM Method)
DHB-AZN-4	Cry-Iso (172 ºC) Iso-N (97.8 ºC)-Cry (31 ºC)
DHB-AZN-6	Cry-Iso (120 ºC) Iso-N (80 ºC)-Cry (32 ºC)
DHB-AZN-8	Cry-Iso (105 ºC) Iso-N (95 ºC)-Cry (31 ºC)
DHB-AZN-10	Cry-Iso (114 ºC) Iso-N (92 ºC)-SmA (74 ºC)-Cry (33 ºC)
DHB-AZN-12	Cry-Iso (93 ºC) Iso-N (81.4 ºC)-SmA (73 ºC)-Cry (33 ºC)

*Cry-Crystalline phase; Iso-Isotropic liquid; N-Nematic phase; SmA-Smectic A phase

2.3.1.4 Photo-switching studies

On exposure to UV light of 365 nm on DHB-AZN-n, it underwent *trans* to *cis* photoisomerization due to the presence of the azo chromophore. The *trans* azo compound shows π-π* transition at 365.2 nm, and *cis* shows n-π* transition at 450.8 nm. On subsequent photoirradiation at 30 s interval, the strong absorbance at 365.2 nm due to the *trans* isomer gradually decreased along with an increase in the absorbance at 450.8 nm due to the increase in the population of the *cis* isomer (**Fig 2.9** and **2.10**). The conversion efficiency from *trans* – *cis* isomer for DHB-AZN-4 is 85.5%, and DHB-AZN-12 is 92.7 %. Further, it was observed that on increasing the spacer chain length, conversion efficiency reaches more than 90 %, which describes the role of the varying spacer length and their potential application in photo-switches and optical data storage devices.

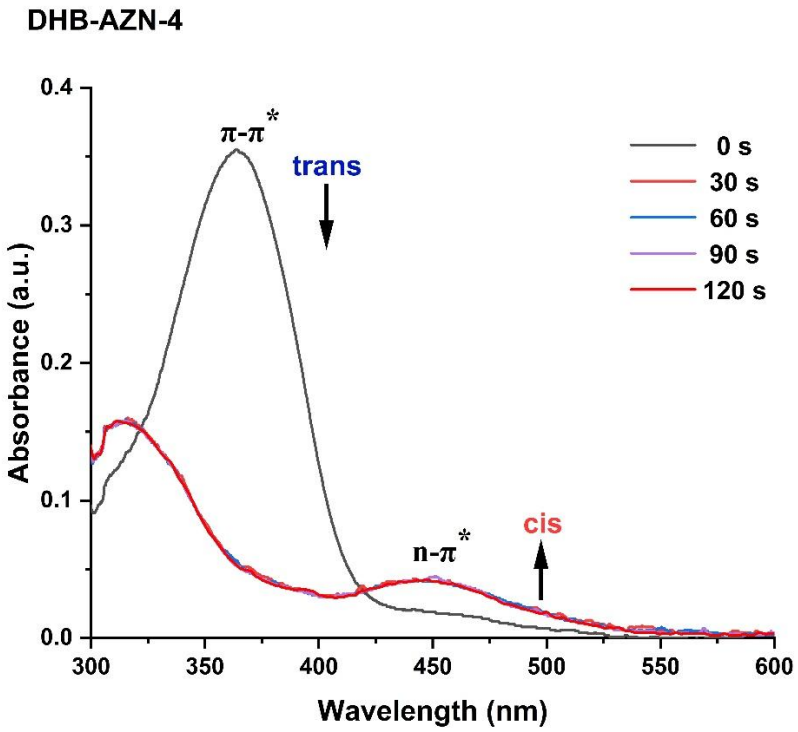


Fig 2.9 UV-vis spectra for *trans-cis* isomerization of DHB-AZN-4.

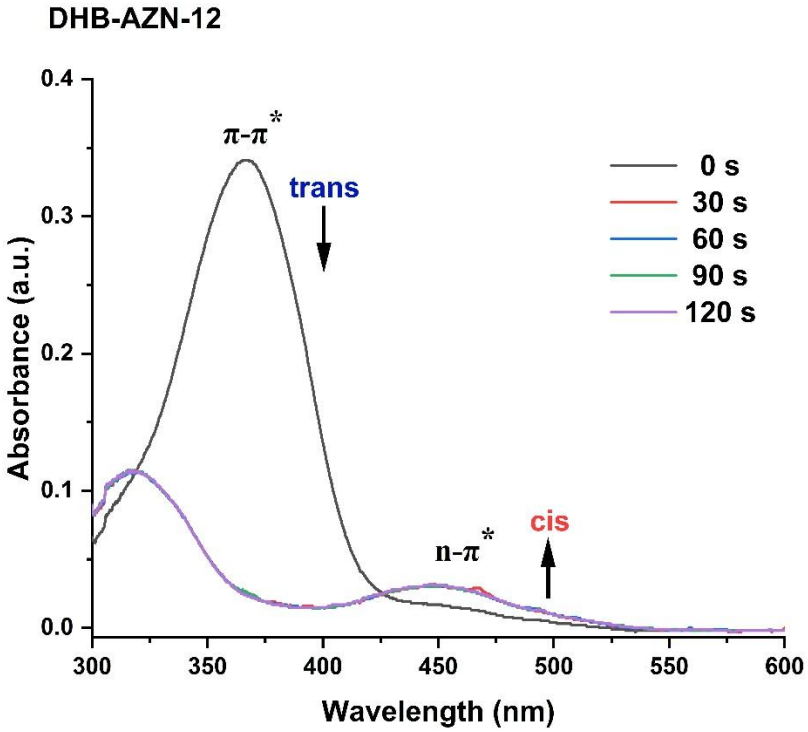


Fig 2.10 UV-vis spectra for *trans-cis* isomerization of DHB-AZN-12.

2.4 Conclusions

A series of ethyl 3,5-bis(4-(4-((*E*)-(4-cyanophenyl)diazinyl)phenoxy)alkoxy)benzoate trimers of varying spacer chain lengths (DHB-AZN-n, n = 4, 6, 8, 10, and 12) were synthesized. The preliminary confirmation of product formation was given by PXRD and FTIR. The structures of the synthesized compounds were further verified by ^{1}H and ^{13}C NMR studies. The POM equipped with hot-stage revealed the monotropic nematogenic behaviour in the cooling cycle for all (n = 4, 6, 8, 10, and 12), unlike the decoxy (n = 10), and dodecoxy (n = 12) derivatives, which exhibited additional smectic A liquid crystalline phase in the cooling cycle. Further, the photo-switching in these synthesized LCTs was analyzed by UV-Vis spectrophotometry by irradiation with 365 nm UV light. All the compounds exhibited excellent *trans-cis* conversion efficiency that exceeded 85 %. In addition, the *trans-cis* conversion efficiency increases with an increase in the spacer chain length. The faster photo-switching in these derivatives enable them as promising candidates for applications in the field of photonics and optoelectronics, especially in fabrication of photo-switchable devices.

2.5 Future Perspectives

- Differential Scanning Calorimetry (DSC), and Thermogravimetric Analysis (TGA) can be performed to further understand the phase transition temperatures and thermal stability of these synthesized compounds, respectively.
- To gain structural insights into the solid state of these compounds, suitable single crystals can be grown and analyzed using single-crystal X-ray diffraction techniques.
- Additionally, device fabrication using these compounds can be undertaken to evaluate their suitability for applications in photo-switches.

2.6 References

1. Kato, T., N. Mizoshita, and K. Kishimoto, *Functional liquid-crystalline assemblies: self-organized soft materials.* Angewandte Chemie International Edition, 2006. **45**(1): p. 38-68.
2. Priestly, E., *Introduction to liquid crystals*. 2012: Springer Science & Business Media.
3. Reinitzer, F., *Beitrage zur Kenntniss des Cholesterins.* Sitzber Akad Wiss Wien Mathnaturw K1 Abt I, 1888. **97**: p. 167-187.
4. Kawamoto, H., *The history of liquid-crystal displays.* Proceedings of the IEEE, 2002. **90**(4): p. 460-500.
5. Nesterkina, M., et al., *Thermotropic liquid crystals in drug delivery: a versatile carrier for controlled release.* European Journal of Pharmaceutics and Biopharmaceutics, 2024: p. 114343.
6. Demus, D., et al., *Handbook of liquid crystals, volume 2A: low molecular weight liquid crystals I: calamitic liquid crystals*. 2011: John Wiley & Sons.
7. Kumar, S., *Chemistry of discotic liquid crystals: from monomers to polymers*. 2016: CRC press.
8. Reddy, R.A. and C. Tschierske, *Bent-core liquid crystals: polar order, superstructural chirality and spontaneous desymmetrisation in soft matter systems.* Journal of materials chemistry, 2006. **16**(10): p. 907-961.
9. Mertelj, A., et al., *Splay nematic phase.* Physical Review X, 2018. **8**(4): p. 041025.
10. Dierking, I., M. Mitov, and M.A. Osipov, *Smectic layer instabilities in liquid crystals.* Soft matter, 2015. **11**(5): p. 819-837.
11. Chilaya, G.S. and L.N. Lisetski, *Cholesteric liquid crystals: physical properties and molecular-statistical theories.* Molecular Crystals and Liquid Crystals, 1986. **140**(2-4): p. 243-286.
12. Andrienko, D., V. Marcon, and K. Kremer, *Atomistic simulation of structure and dynamics of columnar phases of hexabenzocoronene derivatives.* The Journal of chemical physics, 2006. **125**(12).
13. Dierking, I. and S. Al-Zangana, *Lyotropic liquid crystal phases from anisotropic nanomaterials.* Nanomaterials, 2017. **7**(10): p. 305.
14. Martin, J.D., et al., *Metallotropic liquid crystals formed by surfactant templating of molten metal halides.* Nature materials, 2006. **5**(4): p. 271-275.
15. Imrie, C.T., et al., *Liquid Crystal Dimers and Smectic Phases from the Intercalated to the Twist-Bend. Crystals 2022, 12, 1245*. 2022, s Note: MDPI stays neutral with regard to jurisdictional claims in published ….
16. Imrie, C.T. and G.R. Luckhurst, *Liquid crystal trimers. The synthesis and characterisation of the4, 4'-bis [ω-(4-cyanobiphenyl-4'-yloxy) alkoxy] biphenyls.* Journal of Materials Chemistry, 1998. **8**(6): p. 1339-1343.
17. Henderson, P., A. Cook, and C. Imrie, *Oligomeric liquid crystals: from monomers to trimers.* Liquid crystals, 2004. **31**(11): p. 1427-1434.
18. Imrie, C.T. and P.A. Henderson, *Liquid crystal dimers and higher oligomers: between monomers and polymers.* Chemical Society Reviews, 2007. **36**(12): p. 2096-2124.
19. Oikawa, R., et al., *Linear symmetric liquid crystal trimers exhibiting supramolecular chiral architectures.* Soft Matter, 2019. **15**(15): p. 3179-3187.

20. Chan, T.-N., et al., *A crossover from rod-shaped to bent-shaped in symmetric isoflavone liquid crystal trimers exhibiting unusual mesomorphic behaviour.* Journal of Materials Chemistry, 2012. **22**(22): p. 11335-11339.
21. Henderson, P.A. and C.T. Imrie, *Non-symmetric liquid crystal trimers.* Liquid crystals, 2005. **32**(6): p. 673-682.
22. Rahman, M.L., et al., *Synthesis and photoswitching properties of azobenzene liquid crystals with a pentafluorobenzene terminal.* Chinese Chemical Letters, 2014. **25**(12): p. 1611-1614.
23. ashrajbhai Nakum, K., *Synthesis & Characterization of Some Novel Schiff Base Derivatives, Their Metal Complexes and Study of Their Mesomorphic Behavior.* 2021.
24. Achalkumar, A.S., et al., *Non-conventional liquid crystals: synthesis and mesomorphism of non-symmetric trimers and tetramers derived from cholesterol.* Liquid Crystals, 2011. **38**(11-12): p. 1563-1589.
25. Rabari, M., S. Solanki, and A.K. Prajapati, *Novel Magneson-I derived λ-shaped tris azo liquid crystalline trimers.* Dyes and Pigments, 2023. **220**: p. 111757.
26. Dinnebier, R.E. and S.J.L. Billinge, *Powder diffraction: theory and practice*. 2015: Royal society of chemistry.
27. Segneanu, A.E., et al., *Organic compounds FT-IR spectroscopy*. Vol. 145. 2012: InTech Romania.
28. Heinzelmann, H., et al., *Instrumental developments and recent experiments in near-field optical microscopy.* Thin Solid Films, 1996. **273**(1-2): p. 149-153.

2.7 Appendix

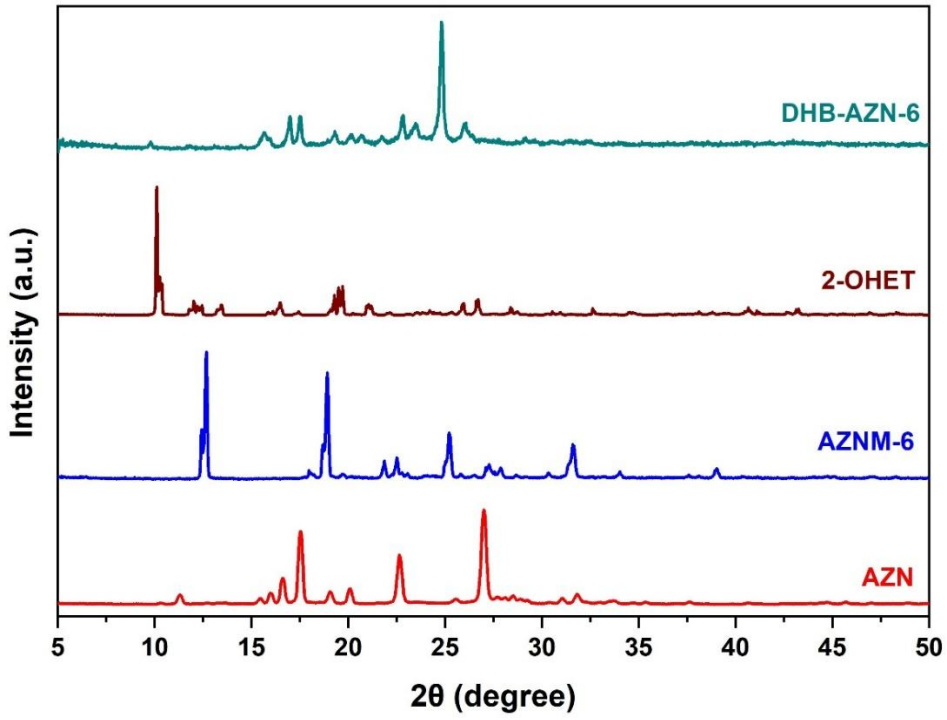


Fig A1 PXRD pattern DHB-AZN-6.

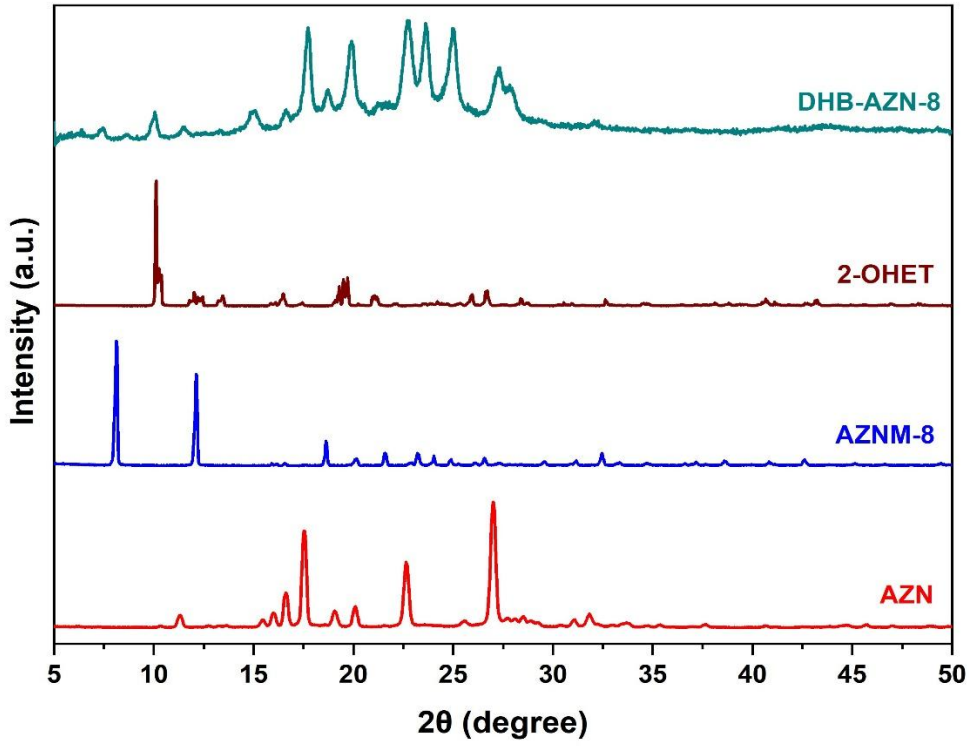


Fig A2 PXRD pattern DHB-AZN-8.

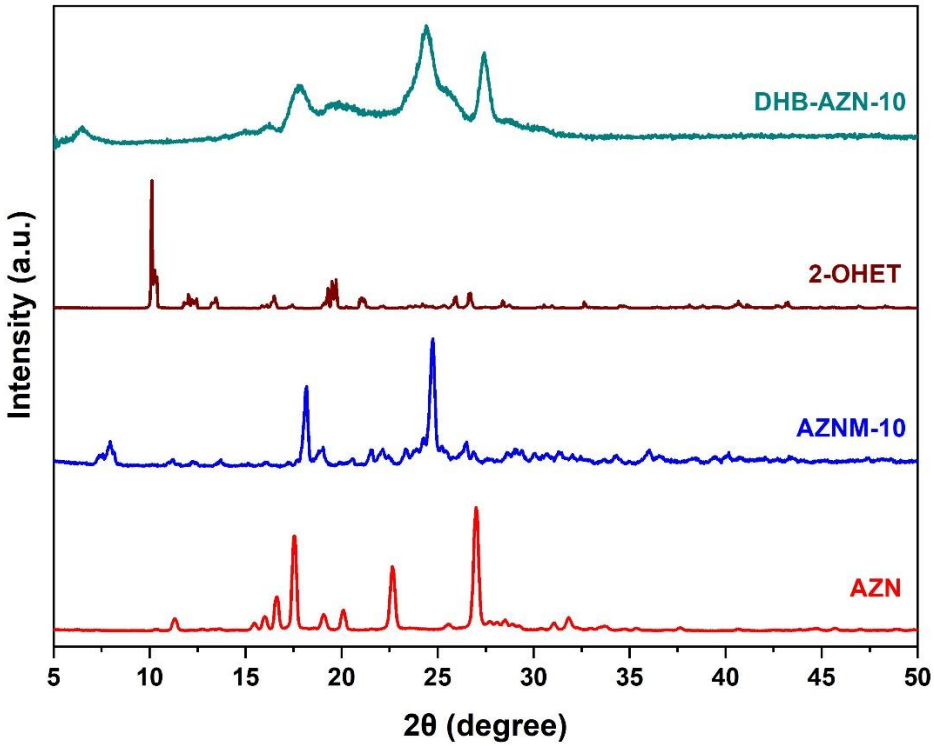


Fig A3 PXRD pattern DHB-AZN-10.

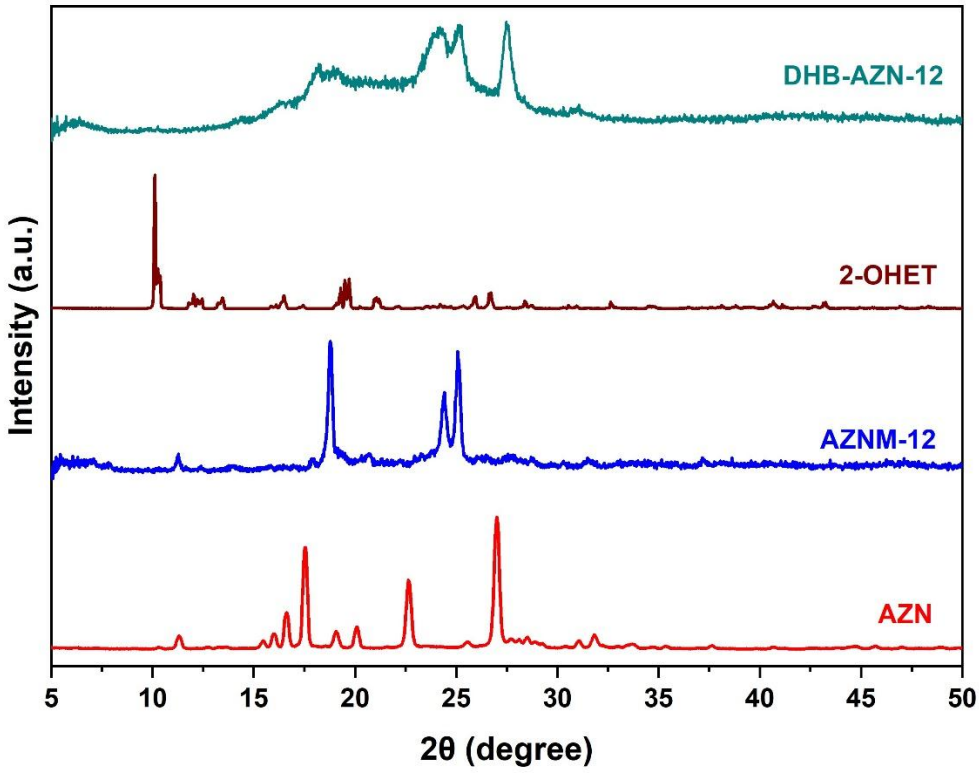


Fig A4 PXRD pattern DHB-AZN-12.

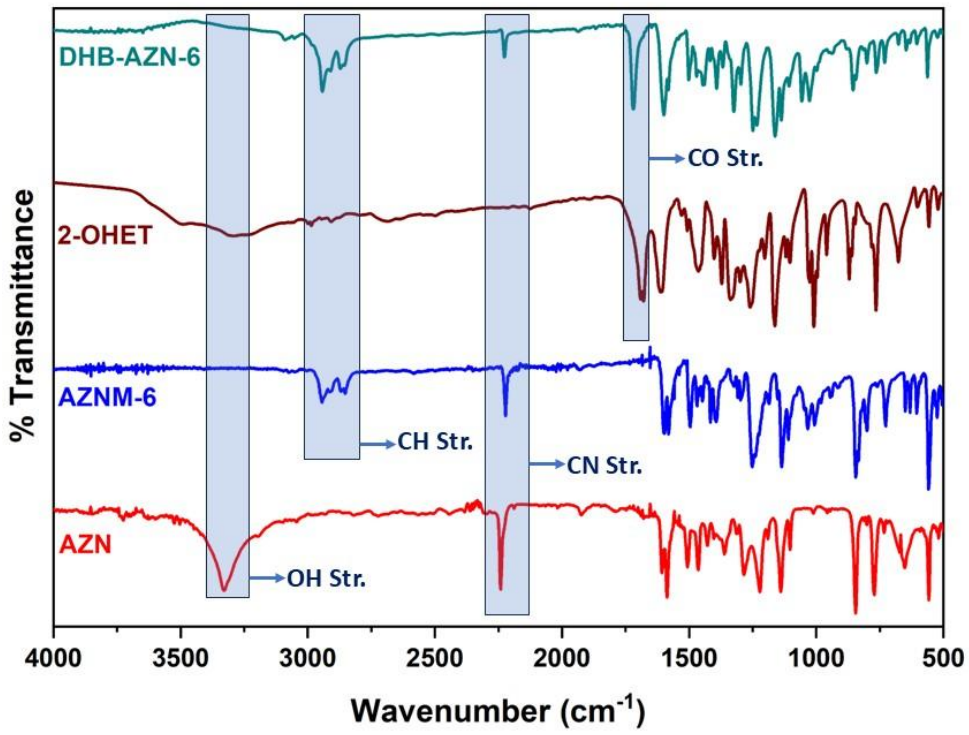


Fig A5 FTIR spectra of DHB-AZN-6.

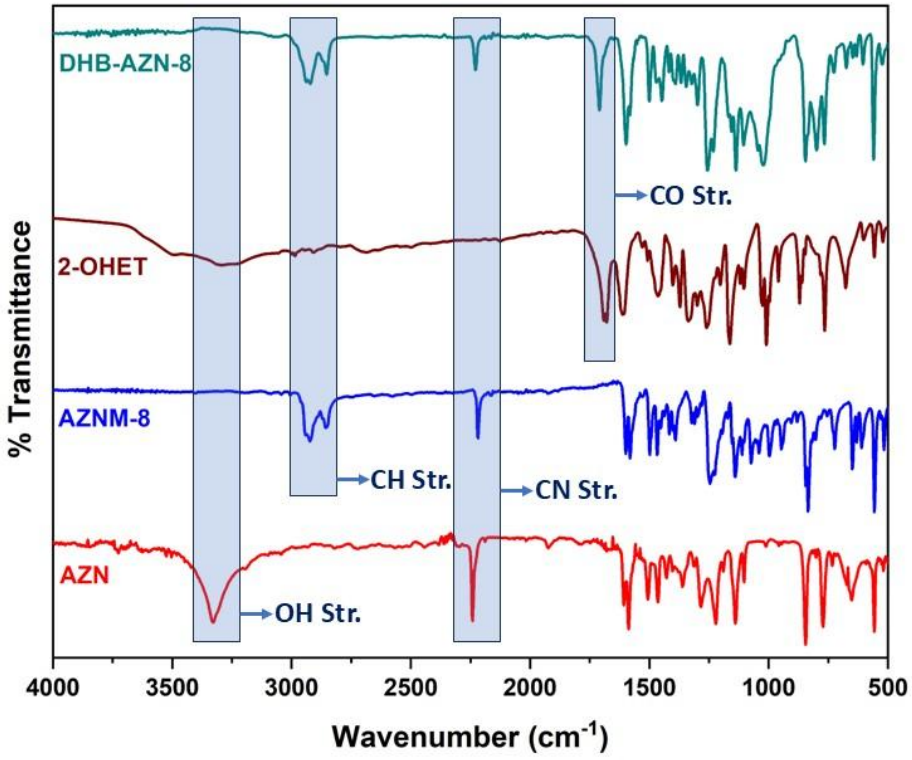


Fig A6 FTIR spectra of DHB-AZN-8.

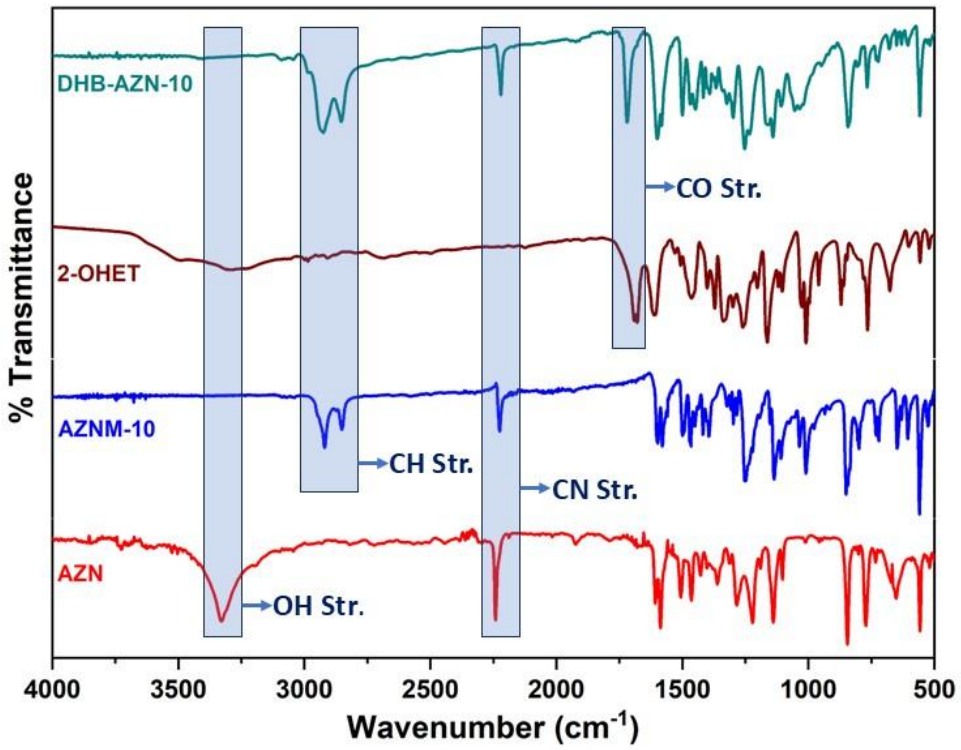


Fig A7 FTIR spectra of DHB-AZN-10.

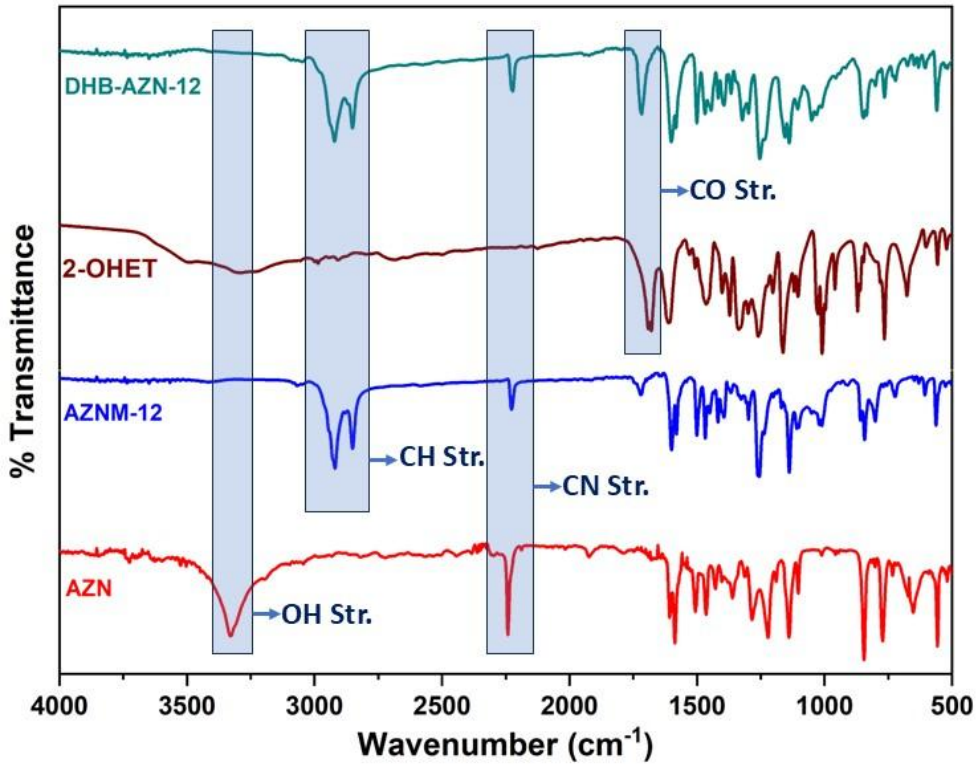


Fig A8 FTIR spectra of DHB-AZN-12.

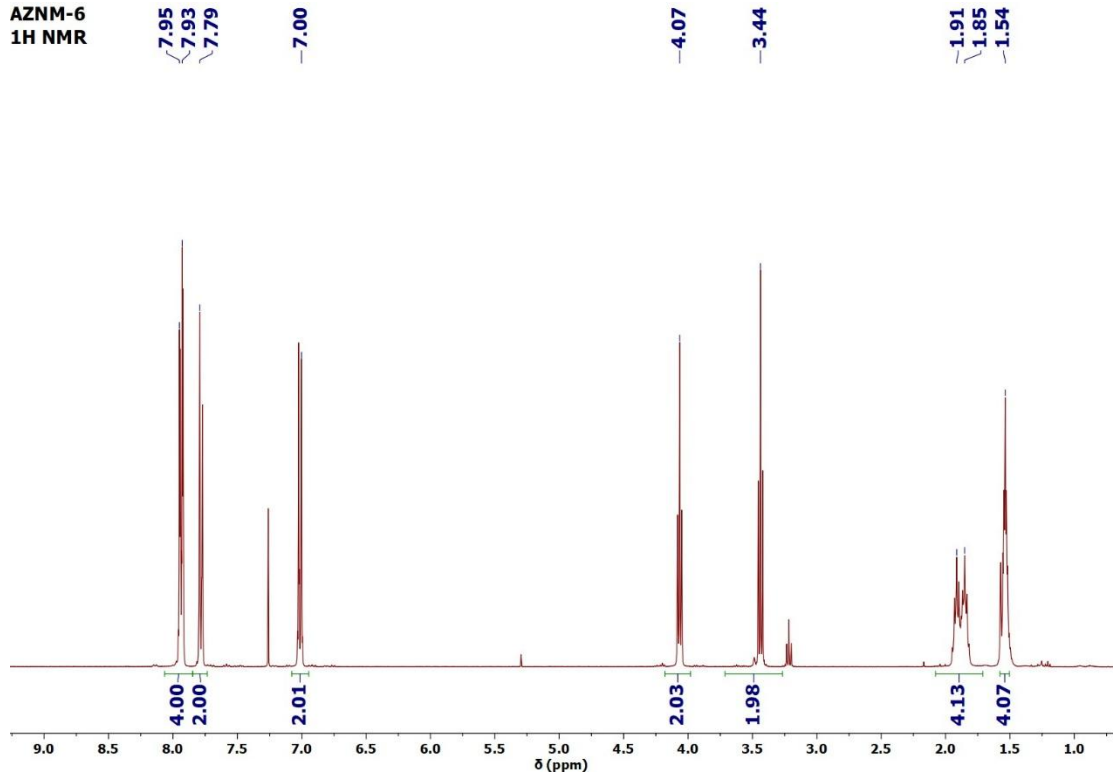


Fig A9 ^{1}H NMR spectra of AZNM-6.

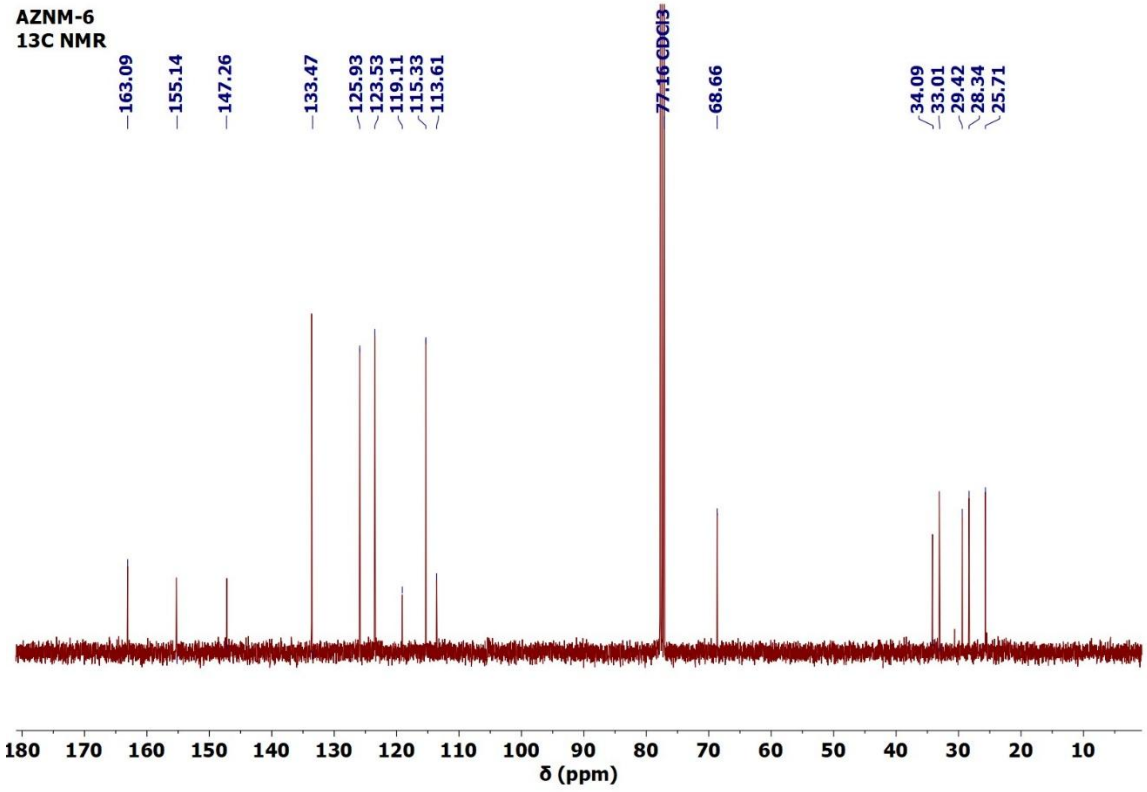


Fig A10 ^{13}C NMR spectra of AZNM-6.

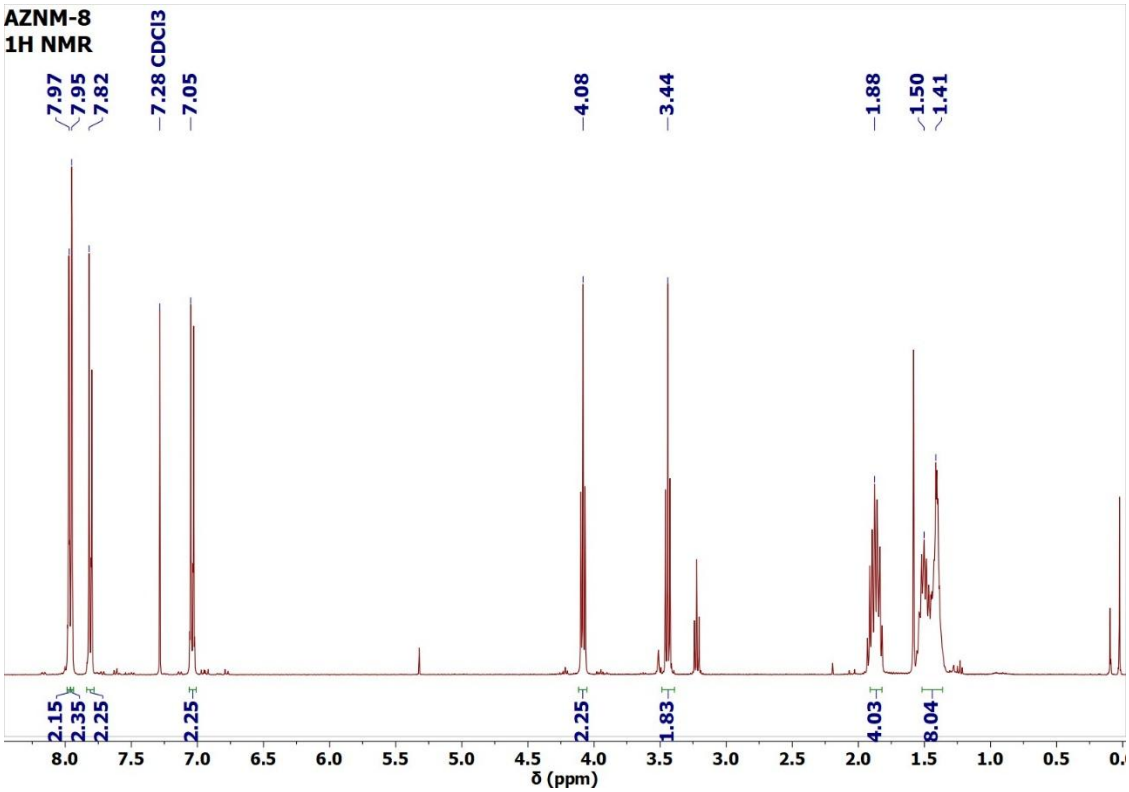


Fig A11 ^{1}H NMR spectra of AZNM-8.

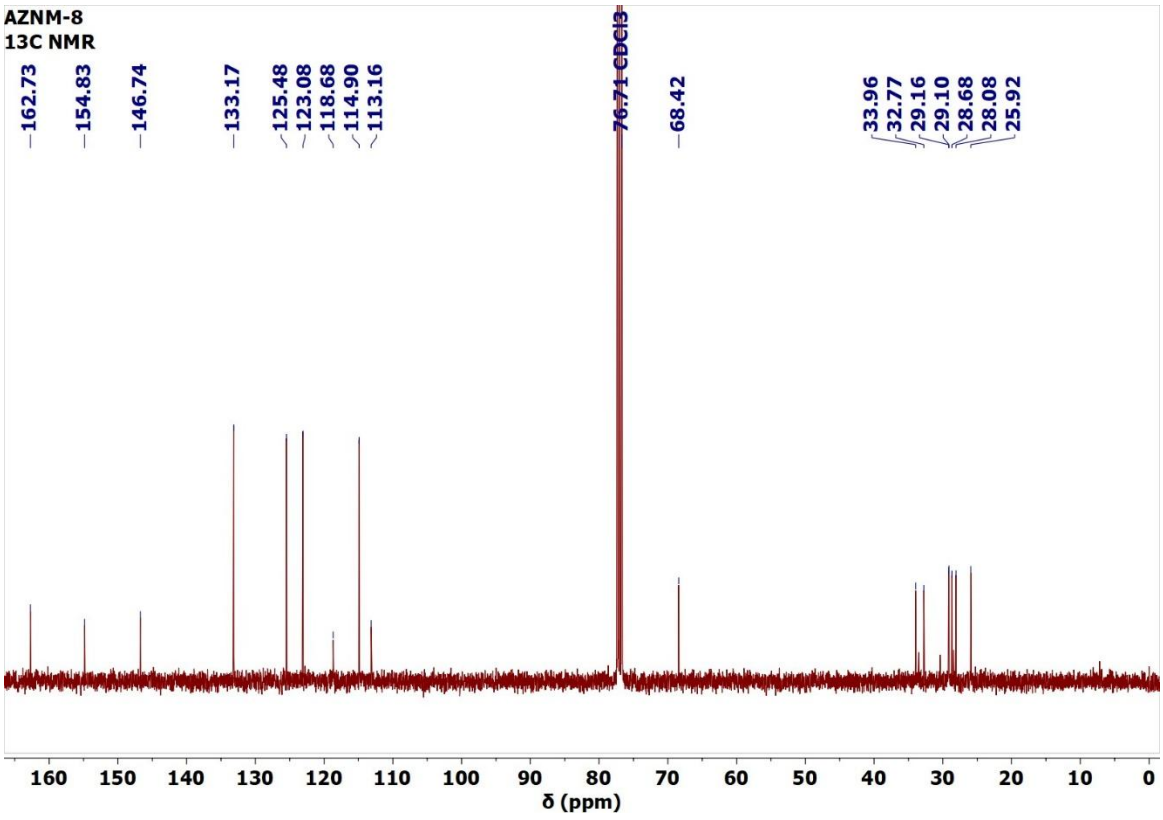


Fig A12 ^{13}C NMR spectra of AZNM-8.

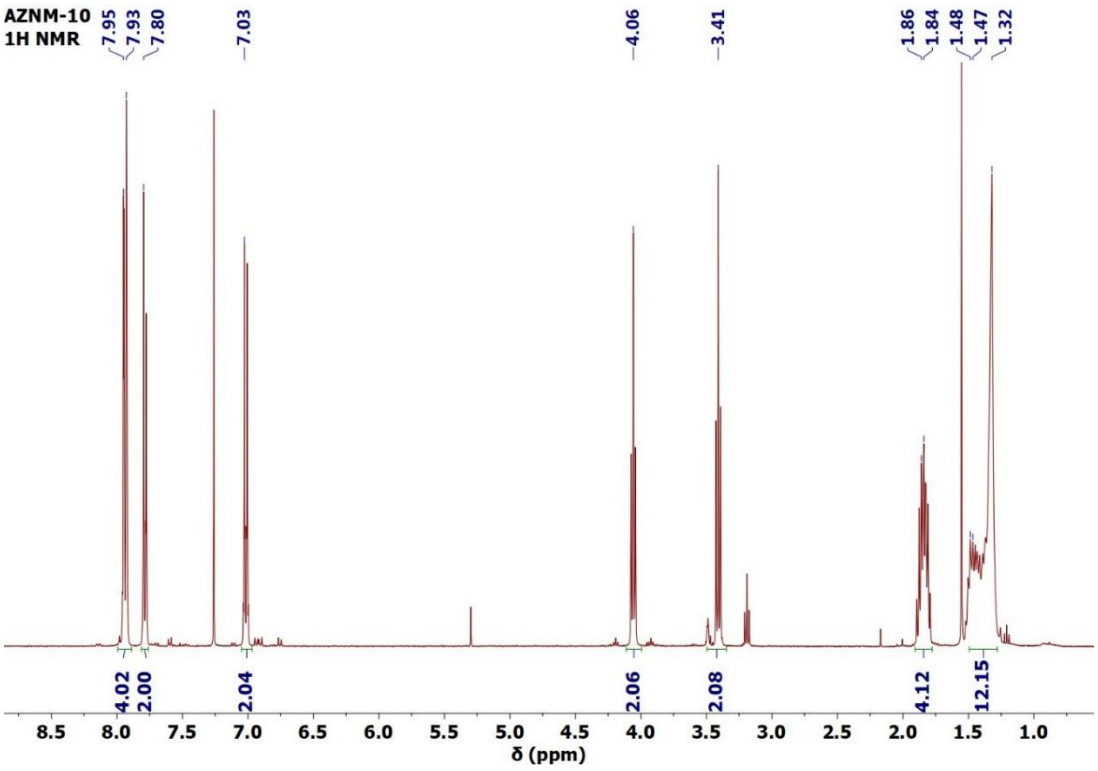


Fig A13 ^{1}H NMR spectra of AZNM-10.

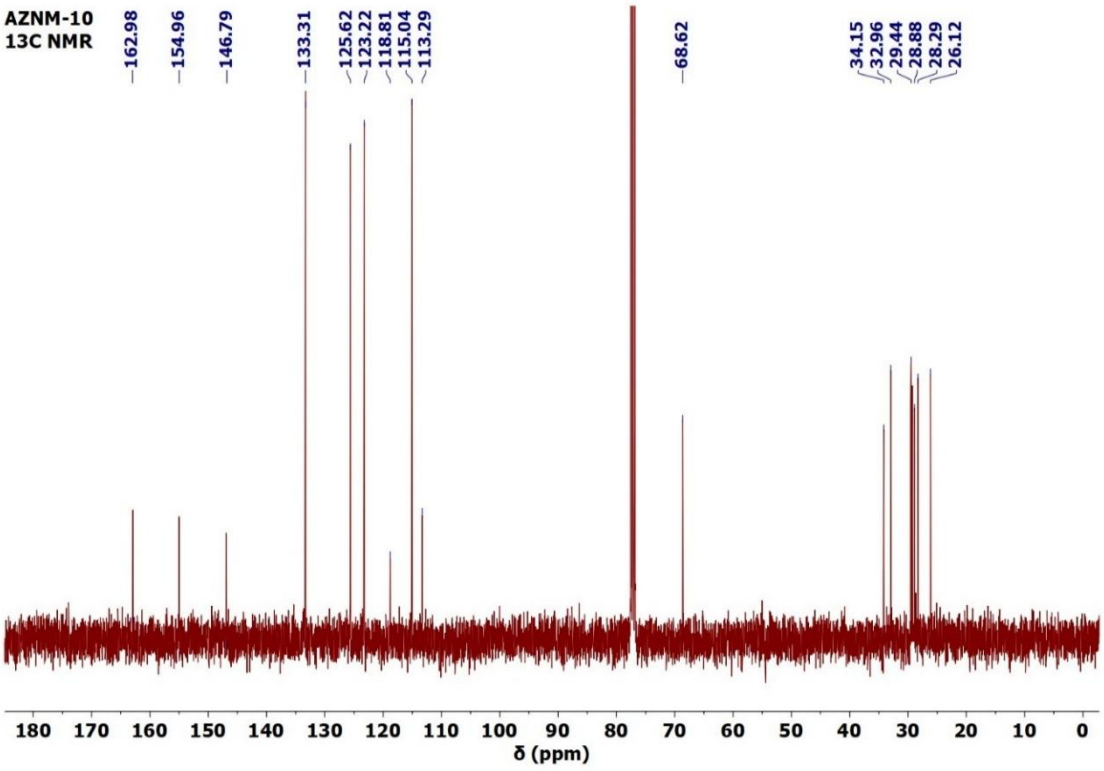


Fig A14 ^{13}C NMR spectra of AZNM-10.

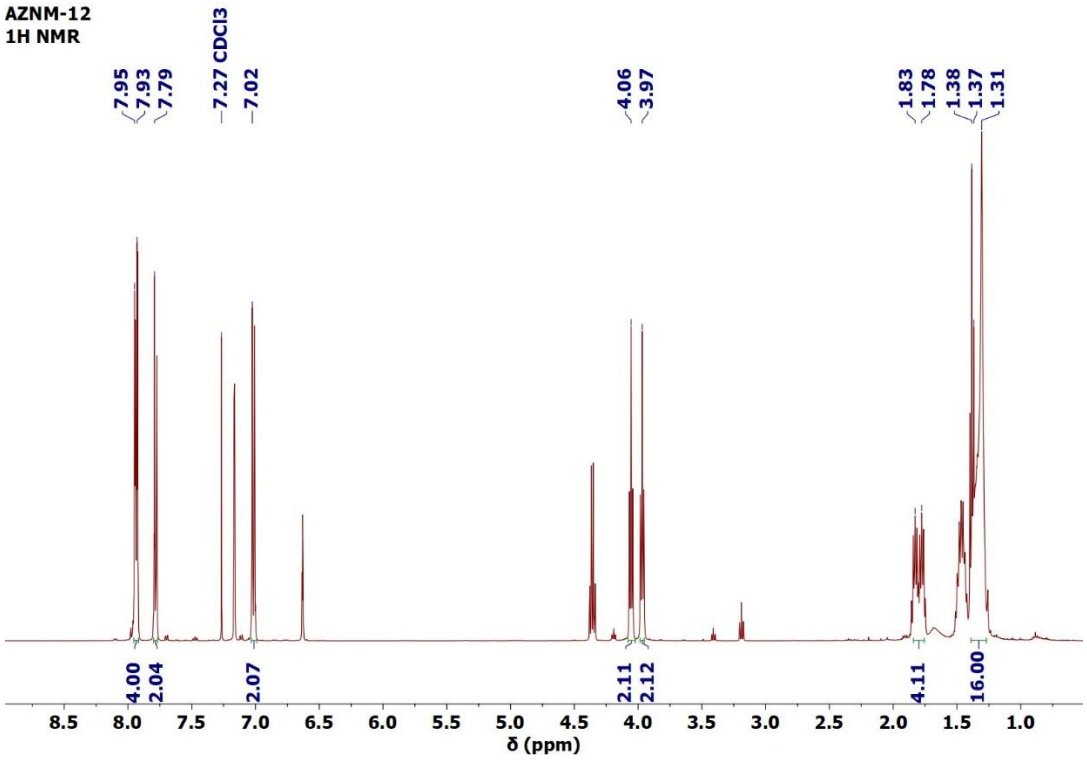


Fig A15 ^{1}H NMR spectra of AZNM-12.

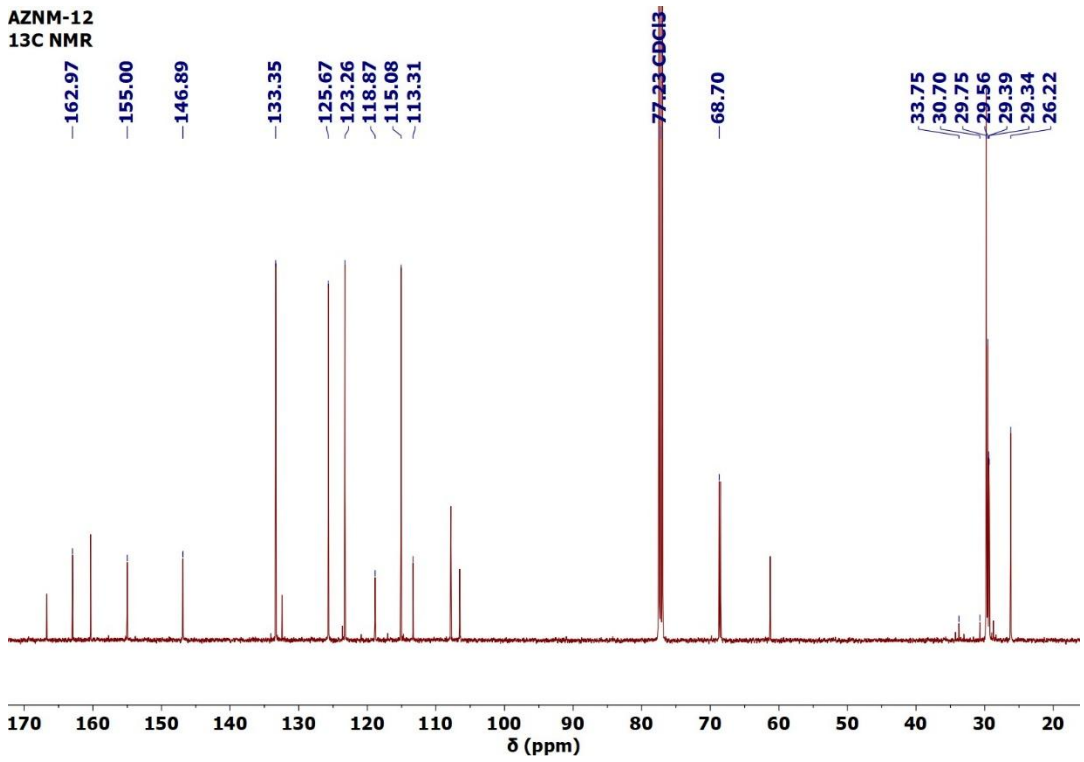


Fig A16 ^{13}C NMR spectra of AZNM-12.

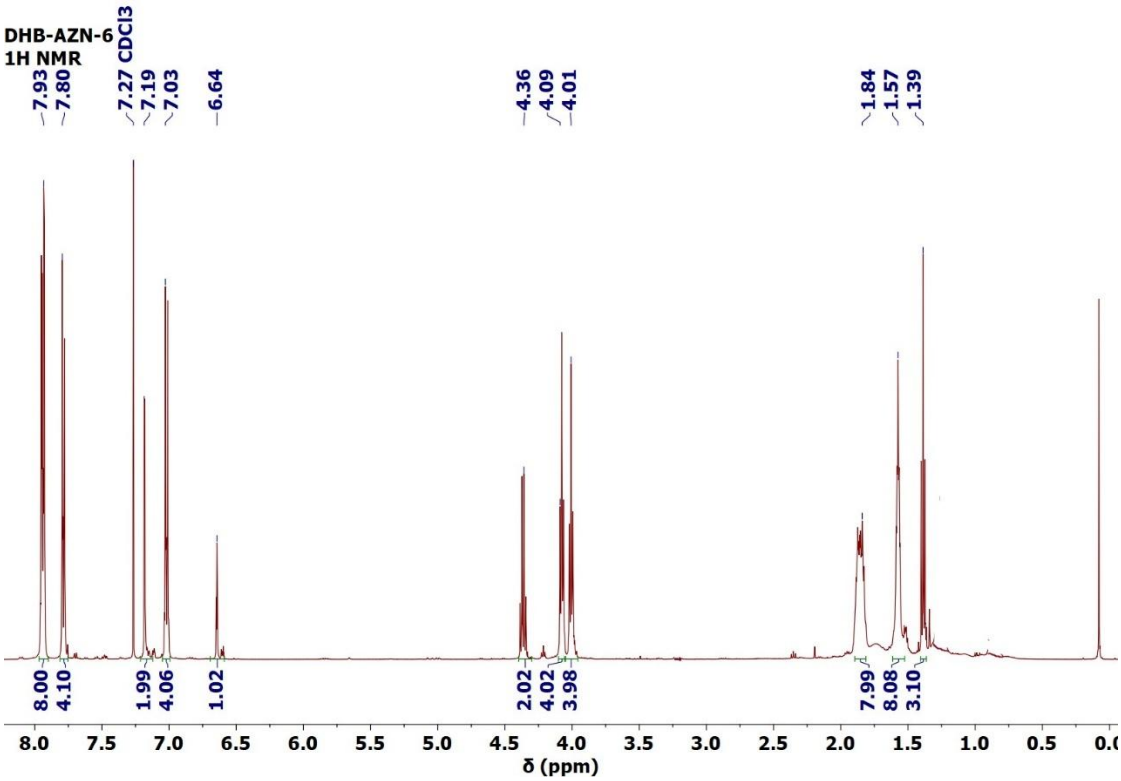


Fig A17 ^{1}H NMR spectra of DHB-AZN-6.

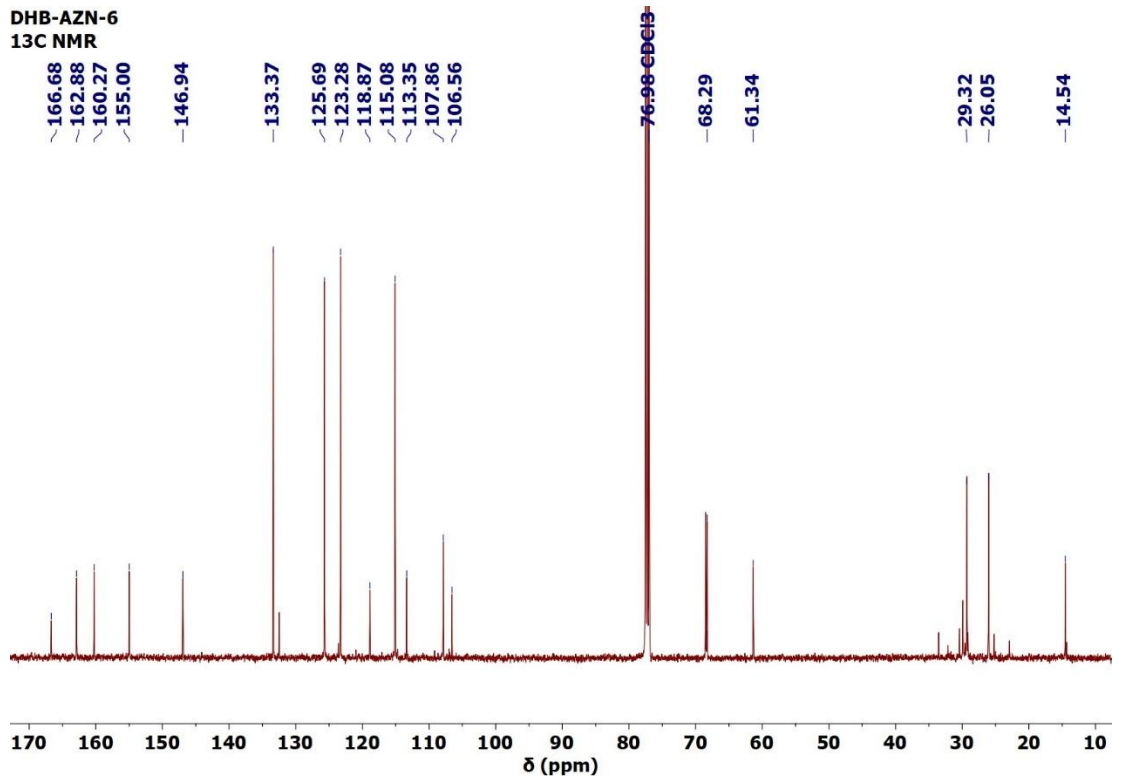


Fig A18 ^{13}C NMR spectra of DHB-AZN-6.

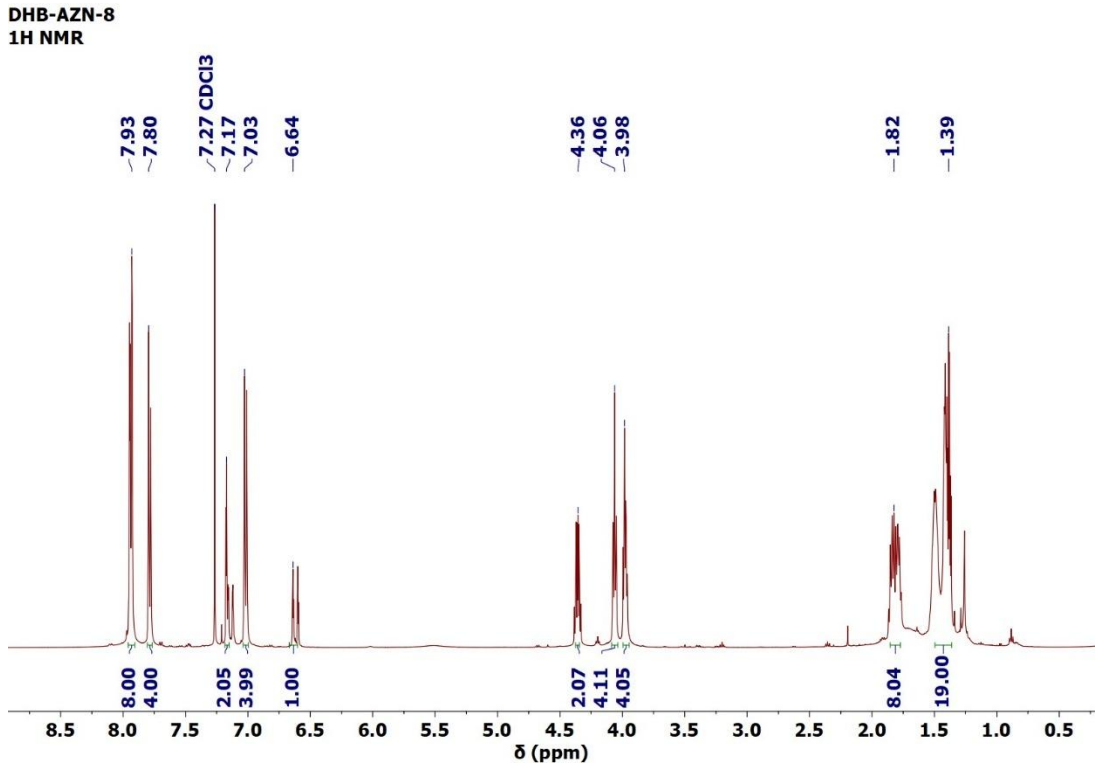


Fig A19 ^{1}H NMR spectra of DHB-AZN-8.

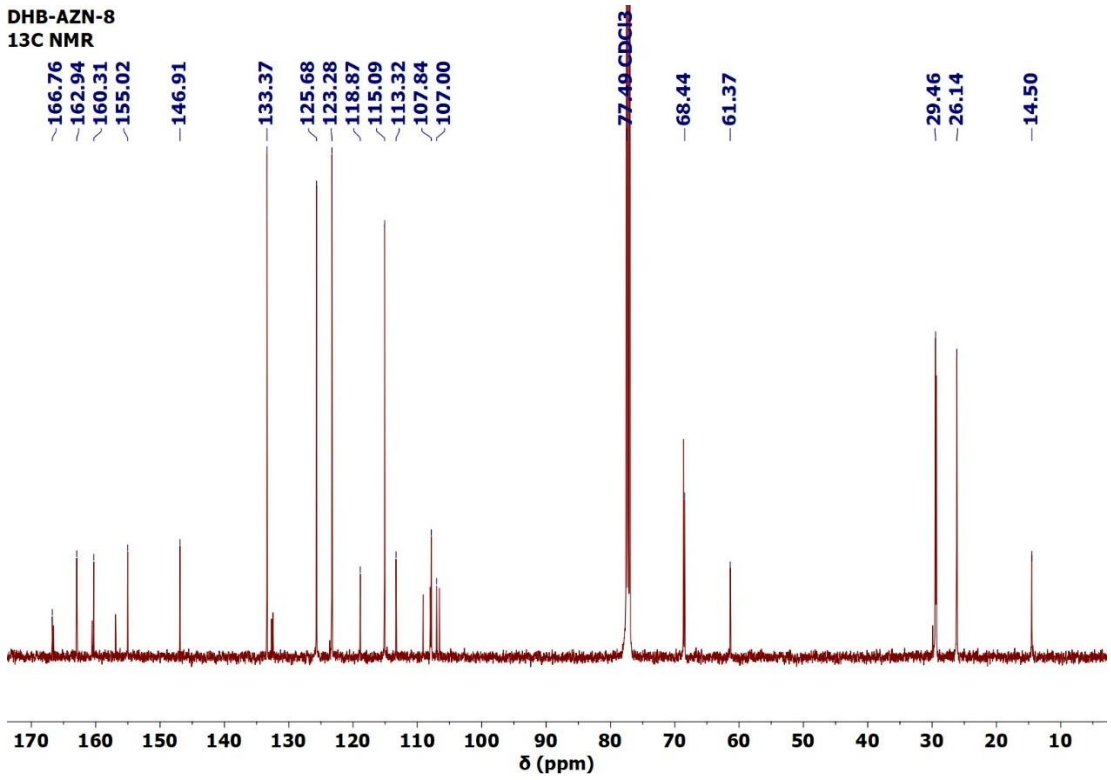


Fig A20 ^{13}C NMR spectra of DHB-AZN-8.

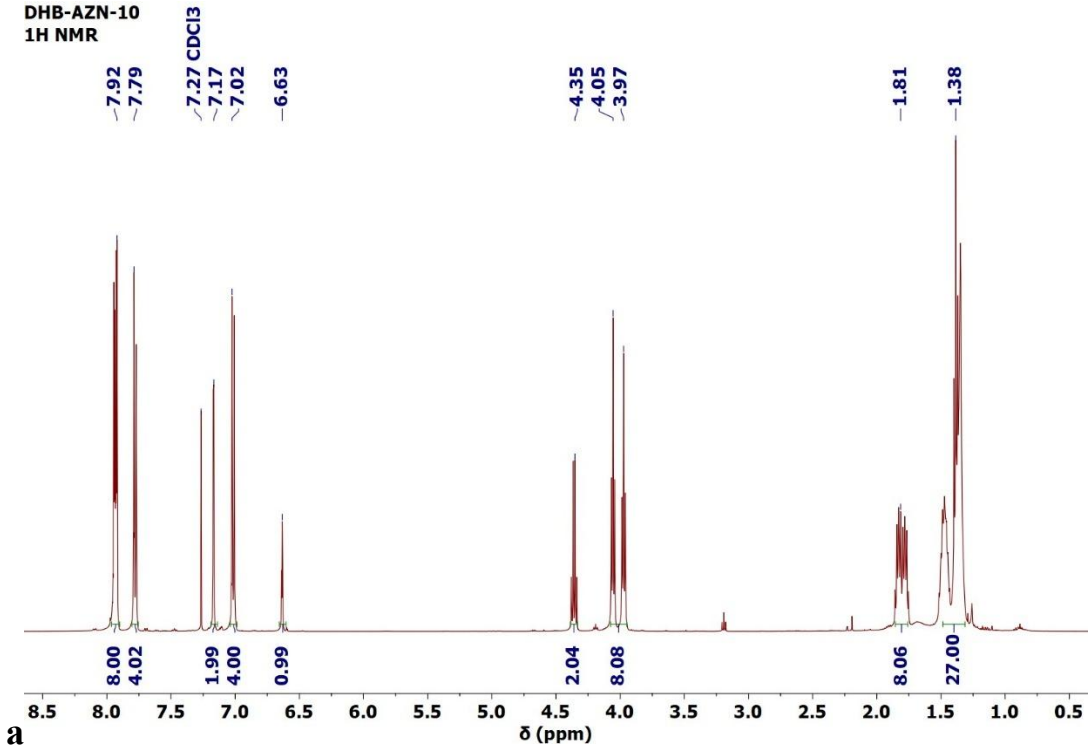


Fig A21 ^{1}H NMR spectra of DHB-AZN-10.

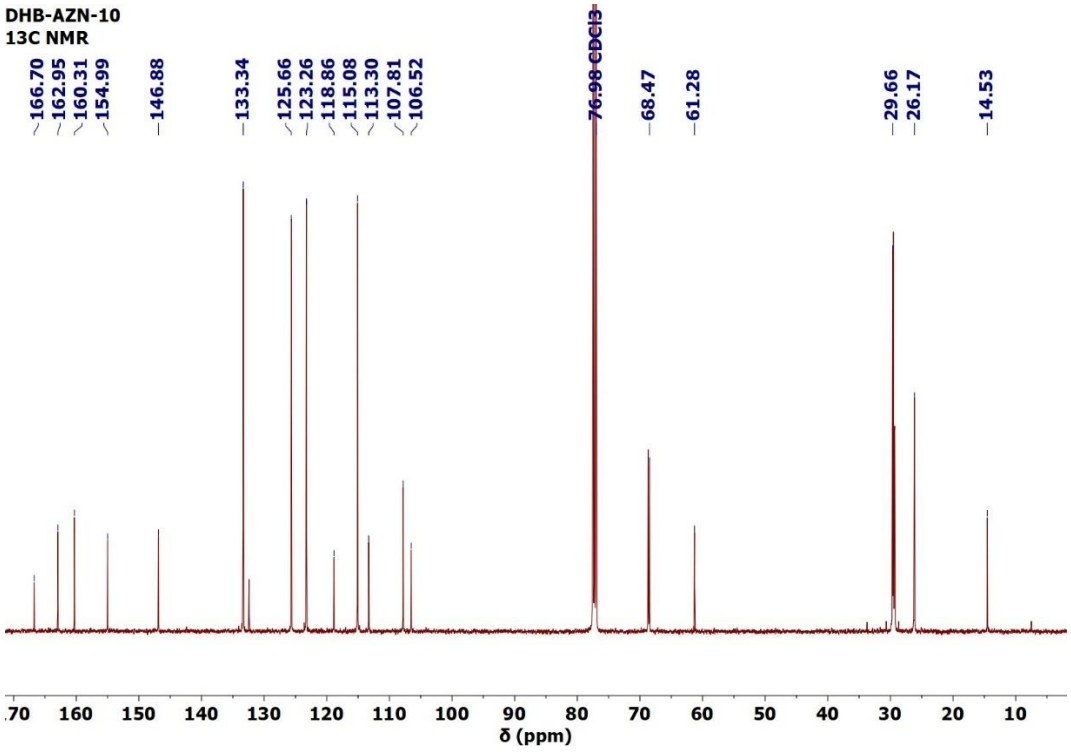


Fig A22 ^{13}C NMR spectra of DHB-AZN-10.

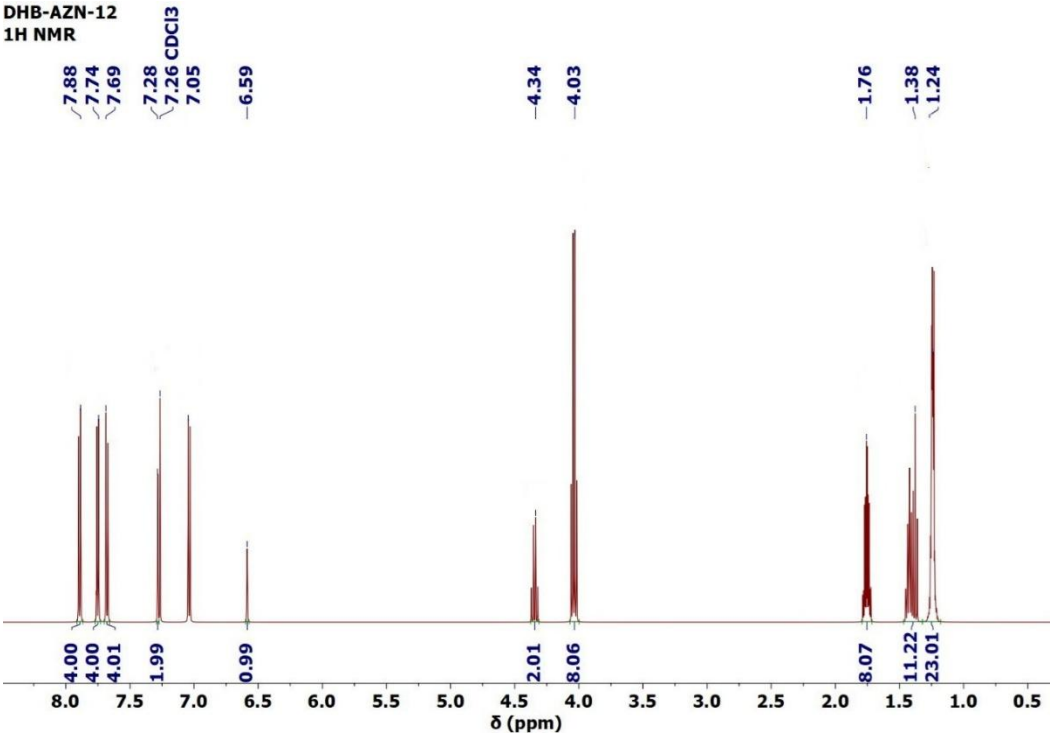


Fig A23 ^{1}H NMR spectra of DHB-AZN-12.

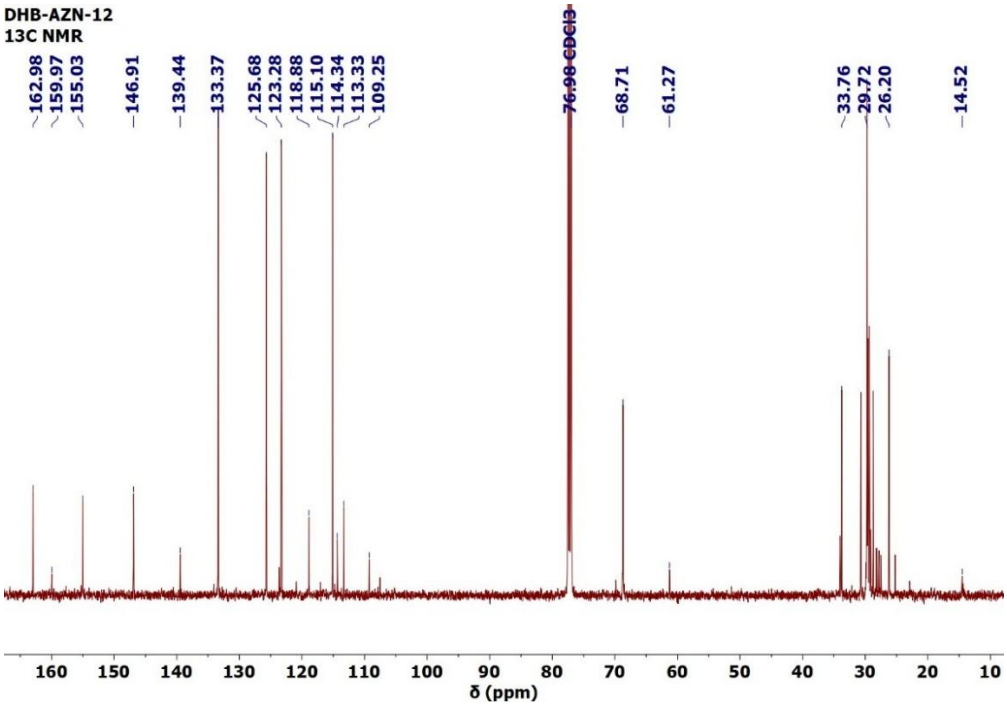


Fig A24 ^{13}C NMR spectra of DHB-AZN-12.